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Collection and Analysis of Nonmethane Hydrocarbon Transport Data from Upwind Ozone Monitoring Sites for Louisville, Kentucky and Nashville, Tennessee

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Collection and Analysis Of Nonmethane Hydrocarbon Transport Data

Louisville, Kentucky and Nashville, Tennessee Ozone Study

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16. ABSTRACT

This document describes the collection of nonmethane hydrocarbon transport data to be used in Level III: EKMA-OZIPP analysis for Louisville, Kentucky and Nashville, Tennessee. Ambient air samples were collected during September, 1980, at sites normally upwind of these cities.

Integrated samples were collected at each site from 6:00 am to 9:00 am daily for two weeks. Samples were collected in Tedlar® bags then transferred to stainless steel canisters for shipment and analysis. Cryogenic trapping with liquid oxygen was used to concentrate the hydrocarbon species and to separate methane and nonmethane hydrocarbons. Nonmethane hydrocarbons were thermally desorbed in a gas chromatograph and quantitated with a flame ionization detector (FID). This method was thoroughly tested and data in support of it are presented within the report.

Nonmethane hydrocarbon (NMHC) concentrations (6-9 am average) near the upwind monitoring site for Louisville, Kentucky, ranged from 0.11 to 0.96 ppmv-C with a mean value of 0.30 ppmv-C and a median of 0.22 ppmv-C. NMHC concentrations near the upwind monitoring site for Nashville, Tennesee ranged from 0.06 to 0.34 ppmv-C with a mean value of 0.12 ppmv-C and a median of 0.09 ppmv-C

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COLLECTION AND ANALYSIS OF NONMETHANE HYDROCARBON DATA

From Upwind Ozone Monitoring Sites for
Louisville, Kentucky and
Nashville, Tennessee

DRAFT FINAL REPORT

December 3, 1980

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ABSTRACT

The purpose of this project was to collect nonmethane hydrocarbon transport data to be used in Level III: EKMA-OZIPP analysis for Louisville, Kentucky, and Nashville, Tennessee. Ambient air samples were collected during September, 1980, at sites normally upwind of these cities.

Integrated samples were collected at each site from 6:00 am to 9:00 am daily for two weeks. Samples were collected in Tedlar® bags then transferred to stainless steel canisters for shipment and analysis. Cryogenic trapping with liquid oxygen was used to concentrate the hydrocarbon species and to separate methane and nonmethane hydrocarbons. Nonmethane hydrocarbons were thermally desorbed in a gas chromatograph and quantitated with a flame ionization detector (FID). This method was thoroughly tested and data in support of it are presented within the report.

Nonmethane hydrocarbon (NMHC) concentrations (6-9 am average) near the upwind monitoring site for Louisville, Kentucky, ranged from 0.11 to 0.96 ppmv-C with a mean value of 0.30 ppmv-C and a median of 0.22 ppmv-C. NMHC concentrations near the upwind monitoring site for Nashville, Tennessee, ranged from 0.06 to 0.34 ppmv-C with a mean value of 0.12 ppmv-C and a median of 0.09 ppmv-C.

This report was submitted in fulfillment of Work Assignment No. 1 of Contract Number 68-02-3513 by Radian Corporation under the sponsorship of the U. S. Environmental Protection Agency. This report covers a period from August 15, 1980, to October 20, 1980.

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SECTION 1

INTRODUCTION

The purpose of this project was to provide information on the transport of nonmethane hydrocarbons as ozone precursors into the cities of Louisville, Kentucky, and Nashville, Tennessee. This information, in combination with other collected data, will be used to prepare revisions to the relevant State Implementation Plans (SIP) using Level III Analysis (1). The approach used to collect the data is compatible with the needs of the EKMA-OZIPP Model. Also, the publication "Guidance for the Collection and Use of Ambient Hydrocarbon Species Data in Development of Ozone Control Strategies", (2) was used as a guide for developing the Work Plan and Quality Control strategies for this project. Finally, the publication "Guidance For Collection of Ambient Non-Methane Organic Compound (NMOC) Data for Use in 1982 Ozone SIP Development, and Network Design and Siting Criteria for the NMOC and NO_χ Monitors", (3) was used as a guide for selecting sampling sites in the areas specified by the Environmental Protection Agency (EPA).

SECTION 2

CONCLUSIONS AND RECOMMENDATIONS

Nonmethane hydrocarbon (NMHC) concentrations (6-9 am average) obtained at a sampling site south of Louisville, Kentucky, between Setpember 16, 1980, and September 30, 1980, ranged from 0.11 to 0.96 ppmv-C. The average of these 6-9 am values was 0.30 ppmv-C and the median 0.22 ppmv-C. NMHC concentrations obtained at a sampling site south of Nashville, Tennessee, between September 19, 1980, and October 2, 1980, ranged from 0.06 to 0.34 ppmv-C, with a mean of 0.12 ppmv-C and a median of 0.09 ppmv-C. The minimum detection limit for NMHC was determined to be 0.025 ppmv-C; precision of duplicate analyses averaged ±6 percent; and the relative accuracy using NBS standards averaged ±8 percent.

Samples were collected near existing upwind ozone monitoring sites. Although upwind sites for both cities conformed to EPA sampling guidelines (3) for hydrocarbon collection, several hydrocarbon sources near the Louisville site potentially could have impacted the NMHC data. However, temporal plots of NMHC concentrations and wind direction for this site did not show any correlations which would indicate local point-source contamination.

Several recommendations can be made concerning the use of Tedlar bags and stainless steel canisters for collection of nonmethane hydrocarbons. When initially purchased, Tedlar bags require a minimum of five 3-hour purges with ultrapure air before they can be used for ambient air sampling. Also, Tedlar bags should be protected from exposure to light at all times. Bags used in this sampling effort were enclosed in cardboard boxes. Tedlar bags which were exposed to sunlight, heat or grossly contaminated samples

continued to leach hydrocarbon contaminants for up to two weeks after exposure.

It is also recommended that sampling systems which are to be used for collection of ambient air should be designed to allow the pump to operate in a moderate flow range. A previous EPA report (2) recommends the use of a critical orifice to reduce pump (Metal Bellows MB-158) flows to rates required for integrated sampling. Experimentation conducted during this project has shown that reducing the pump output in this manner for more than 30 min. causes excessive heating of the pump which results in low-level (0.1-0.5 ppmv-C) contamination of the sample. For this project the pump output was split and two flow restrictors were used to regulate the sample collection and total pump flow. This system provided very constant sampling flow rates and did not produce excessive pump heating. It is also recommended in the EPA report mentioned above (2) that ultrapure air should be pumped through the entire sampling system before and after sample collection, and then analyzed. In the present case it was found that although 30 min. sampling blanks produced no contamination, sampling blanks collected for 3 hours did show contamination; presumably due to excessive pump heating. Therefore, it is also recommended that as a quality control measure, blanks should be collected by pumping ultrapure air through the entire sampling system for a length of time equal to that of sample collection.

Since the Level III analysis requires only total nonmethane hydrocarbon data, hydrocarbon speciation is not required. However, when this project was initiated the only method available for measurement of total nonmethane hydrocarbons was continuous NMHC analyzers, which are unreliable at concentrations below 1.0 ppmv-C. It was recommended in a previous EPA report (2) that this type of data should be obtained chromatographically, using two separate chromatographic columns. This is a very time consuming and expensive method for acquiring the type of data required. A method was developed specifically for the determination of total nonmethane hydrocarbon content as part of this work. This method proved to be very reliable and the short

analysis times allowed multiple analyses of the samples collected for this project. The method discussed in this report provided an accurate, cost-effective means of acquiring NMHC data and is recommended for future applications of this type.

SECTION 3

ANALYTICAL SYSTEM

The Level III Analysis: City-Specific EKMA Model requires nonmethane hydrocarbon data to provide information on upwind ozone precursors. Because of the imprecision of continuous THC/CH_4 analyzers at ambient nonmethane hydrocarbon levels, the EPA has recommended that the NMHC data be acquired by collecting grab samples and analyzing these chromatographically (2). Since hydrocarbon speciation was not required, the analytical system was designed without a chromatographic column. This provided rapid analysis times resulting in an accurate, cost-effective method for acquiring the NMHC data.

Description

A schematic diagram of the analytical system is presented in Figure 1. The chromatograph used was a Tracor 560 equipped with a flame ionization detector. The signal from the chromatograph was processed with a Hewlett-Packard® 3388 Integrating Computer. The system's plumbing was controlled by a Valco® stainless steel 10-port valve which was mounted inside the chromatograph oven. All flow lines were 1/8 in. o.d. stainless steel with the exception of the line from the 10-port valve to the FID which was 1/16 in. o.d. stainless steel. Gas input to the system was controlled by two 3-way valves which allowed selection of gas standards, samples, or ultrapure nitrogen purge gas. All flow through the system was by means of positive pressure in the external gas cylinders. The sample trapping loop consisted of 4 in. of 80/100 mesh glass beads packed in 1/8 in. o.d. stainless steel tubing. Cryogenic trapping was achieved by cooling the trap in liquid oxygen. Trapped hydrocarbon species were thermally desorbed with boiling

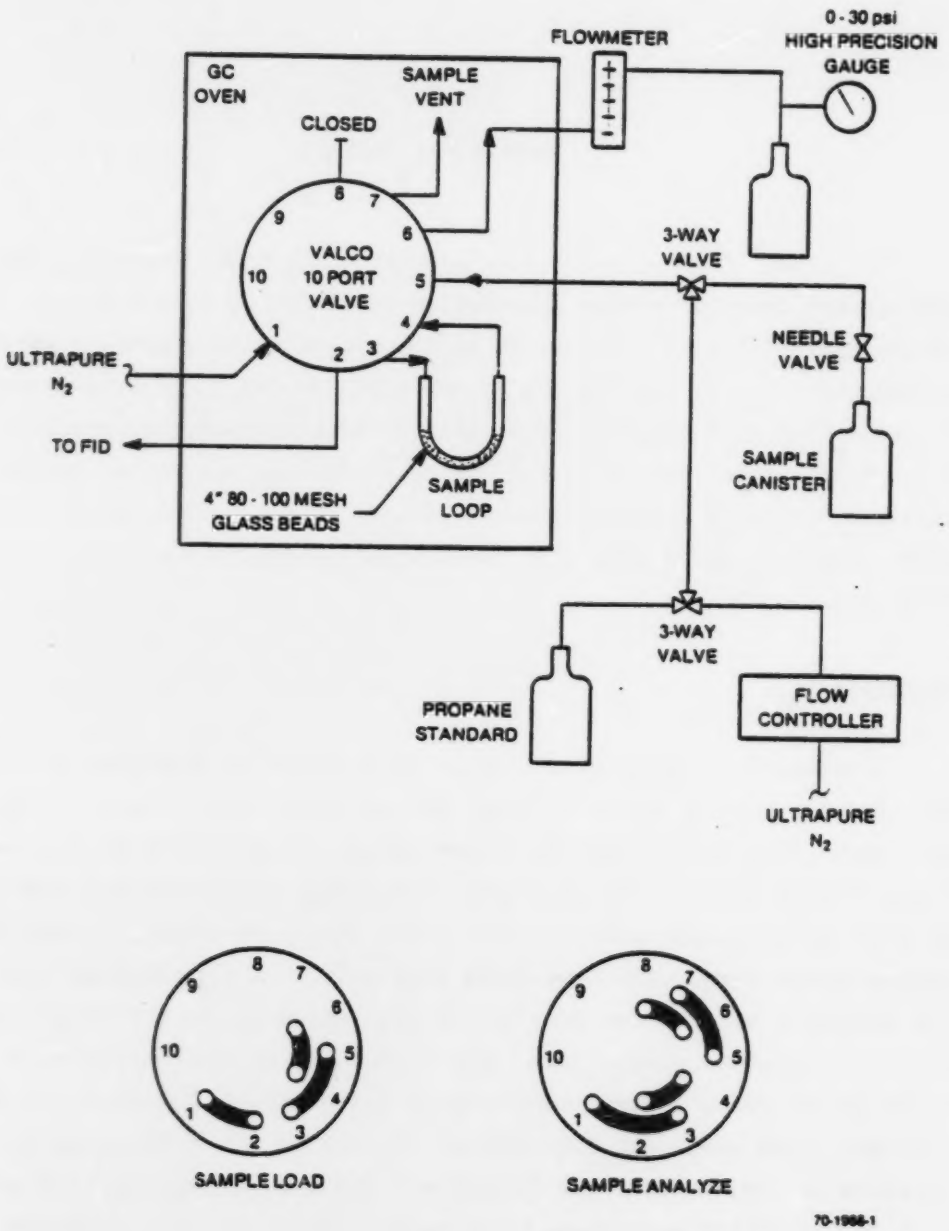


Figure 1. Schematic of Analytical System.

water. The volume of sample passed through the trap was measured by collecting the gas in a 2.8 L reservoir and monitoring the pressure of the reservoir with a high precision pressure gauge (Airco No. 60010). A flow meter was situated between the 10-port valve and sample reservoir to monitor flowrate through the loop. Sample flow was controlled with a needle valve situated in the sample inlet line.

The analysis procedure was initiated with the 10-port valve in the "analyze" position. In this position the ultrapure nitrogen carrier flowed through the sample loop to the FID and sample flow was vented to the atmosphere. Prior to sample loading, the loop was cooled with liquid oxygen for two minutes and the sample intake lines were purged. After two minutes the 10-port valve was switched to the "sample load" position and flow was routed through the cryogenic trap and into the sample reservoir. When the desired pressure was reached, the 10-port valve was switched back to "analyze" and the computer program initiated. After a one minute delay period, the liquid oxygen was removed and boiling water was placed on the trap. Runs were allowed to proceed for five minutes. The purpose of the one minute delay was to allow the FID time to stabilize from the pressure surge and to remove any methane which may have collected on the trap.

Computer integration of peak areas was begun when the hot water was placed on the trap. Upon termination of a run all peak areas were summed and the final pressure was entered into the computer by the operator. The total peak area was applied against the most recent calibration data by the computer and a hydrocarbon value was calculated.

The 10-port valve and sample loop were situated in the GC oven to allow rapid thermal cleaning. During use the oven was maintained at 60°C to prevent condensation in the valve or tubing. When not in use, the oven was maintained at 100°C with the valve in the "load" position and the sample loop purged by ultrapure nitrogen at 15 mL/min. Occasionally, when samples with high water content were analyzed, a small broad peak was observed to

elute well after the hydrocarbon peaks. This peak was not reproducible and appeared to be a material which collected in the system. This peak was not integrated and when it was observed the system was purged for 15 minutes with ultrapure nitrogen at 50 mL/min with the oven at 130°C. The oven was then cooled and analyses continued.

Calibration

Calibration was achieved using a NBS traceable 0.094 ppmv propane standard. Four point calibration curves were prepared by analyzing 100 to 500 mL volumes of the standard. The data were then treated by at least squares linear regression analysis and the slope, y-intercept, correlation coefficient, and standard error were calculated and stored by the computer. If the correlation coefficient was less than 0.99 the system was heated and purged, then recalibrated. Calibrations were run before and after each set of sample analyses.

Method Validation

The analytical system was tested to determine response to various carbon compounds, efficiency of separation of methane, effect of flow rate through the cryogenic trap, and effect of humidity. Parameters including detection limit, reproducibility, and linearity were also evaluated.

Hydrocarbon Response

Response of the analytical system to different carbon compounds was evaluated with standards of methane, ethane, propane, and a mixture of C_2-C_6 n-alkanes. The system was calibrated with each of these by passing volumes from 50 to 1000 mL of respective gas standards through the trap. Calibrations for these compounds are shown in Figure 2. Linear calibrations were obtained for up to one liter of propane or the C_2-C_6 n-alkane mixture. A linear calibration was obtained for ethane at low analysis volumes but

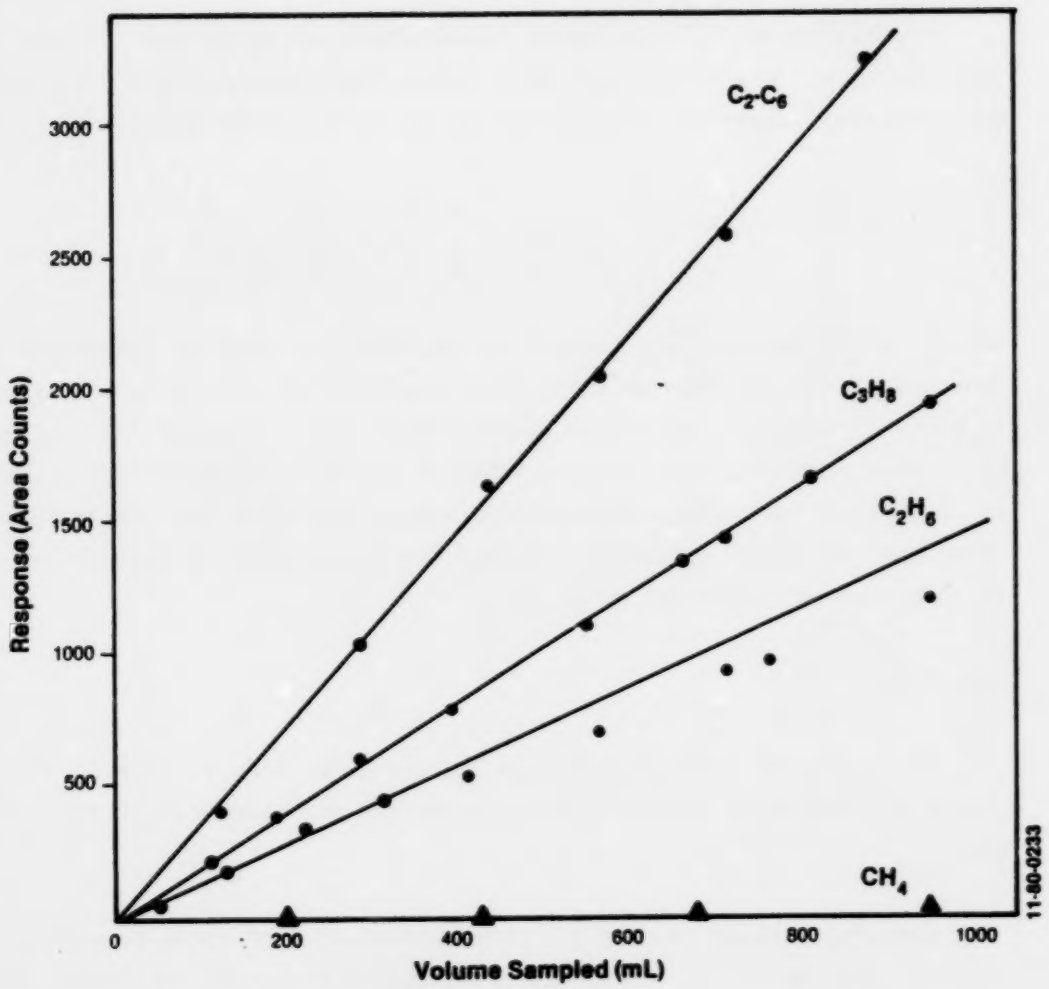


Figure 2. Response to Various n-Alkanes - Ethane at 0.188 ppmv-C, Propane at 0.282 ppmv-C, C_2-C_6 n-Alkane Mixture at 0.529 ppmv-C.

some losses of this compound were observed when volumes above 400 mL were used. This was probably not observed in the alkane mixture since ethane comprised only 10 percent of the carbon content in this case. Methane gave no response at volumes below 700 mL and only a slight response at 1000 mL.

The slopes of the hydrocarbon calibrations are presented in Table 1. Also listed are the effective carbon number contributions, ECNC, for each gas standard. These were calculated using the following equation:

$$ECNC = \frac{R_x\ C_s}{R_s\ C_x}$$

where: R_x is the response (slope) to the standard which is propane in this case, R_s is the response to the sample compound, and C_x and C_s are concentrations of standard and sample, respectively. An equivalent FID response to all carbon compounds will produce ECNCs of 1. In the present case, ECNC values for the nonmethane hydrocarbons agreed to within four percent, which justifies the use of a propane standard for quantitative evaluation of total nonmethane hydrocarbon content.

Flow Rate

The effect of flow rate through the cryogenic trap on trapping efficiency was evaluated using standards of ethane and propane, each at 0.094 ppmv.

Constant volumes of each gas were sampled at flow rates from 25 to 200 mL/min. Results of this study are presented in Figure 3. Different flow rates in the range tested appeared to have no effect on trapping efficiency. The coefficient of variation for responses obtained for ethane at various flows was one percent and three percent for propane. Also, the average response for propane was 1.6 times that of ethane (1.5 x theoretical), again demonstrating the response to carbon content.

TABLE 1. CALIBRATION SLOPES FOR HYDROCARBON SPECIES

Compound	Concentration (ppmv-C)	Slope (area/L)	ECNC[1]
Methane	3.20	90	0.004
Ethane	0.188	1370	1.006
Propane	0.282	2040	1.000[1]
C_2 - C_6	0.529	3670	0.960

[1] = Effective Carbon Number Contribution using propane as reference

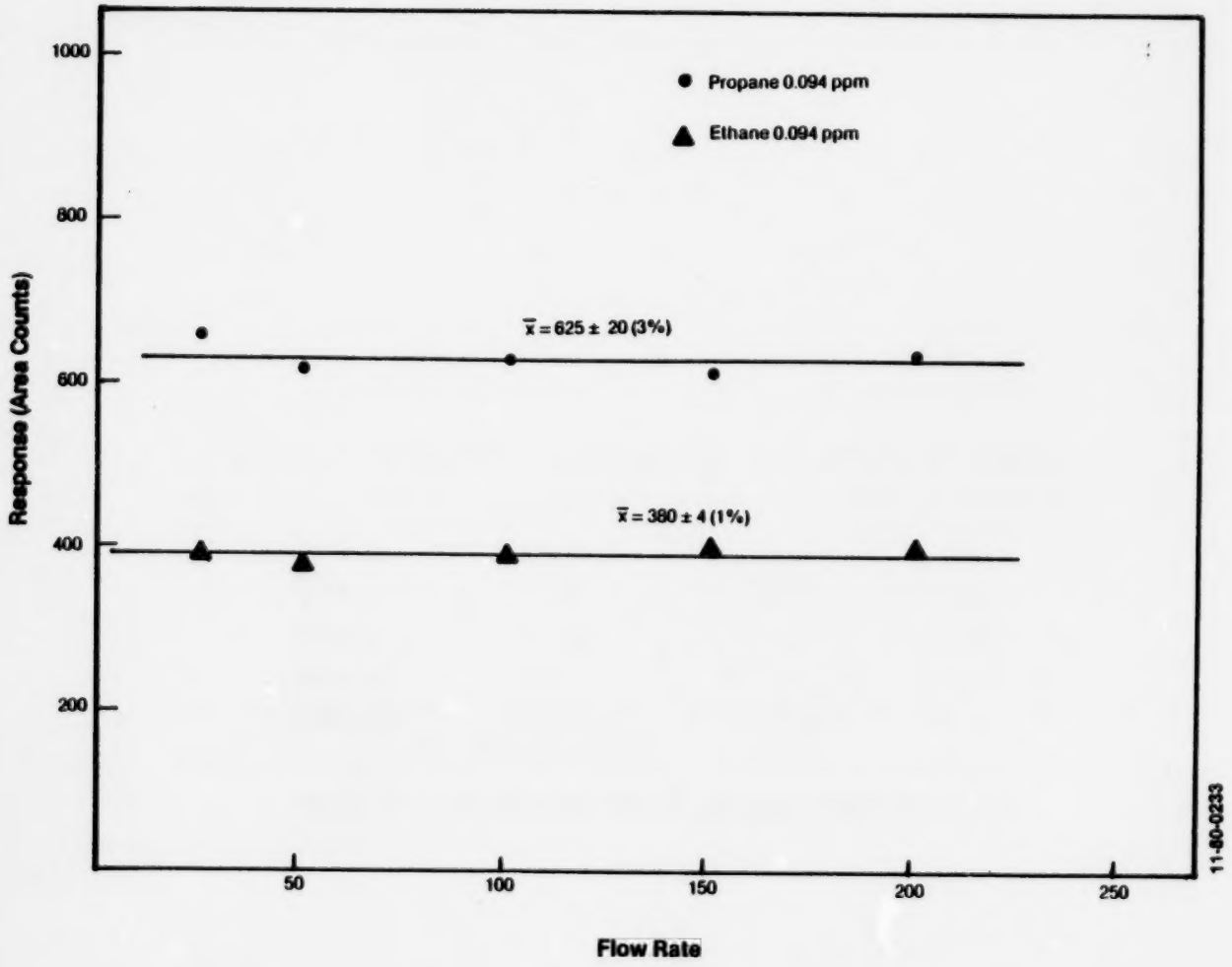


Figure 3. Effect of Flow Rate on Trapping Efficiency of Propane and Ethane.

Moisure Effect

The effect of water on the analytical system was also studied. Water could have several effects including clogging the cryogenic trap, increased trapping of methane or decreased trapping of other hydrocarbons, and suppression of FID response. Mixtures of gases were prepared by diluting a 0.94 ppm propane standard with ultrapure air, a percentage of which was bubbled through the water. Water content of the gas mixtures was controlled by proportionally varying the amount of air which was bubbled through the water. Although moisture contents prepared in this matter are not exactly analogous to relative humidity, any effects due to increasing moisture content would be observed.

The results of this study are presented in Figure 4. Some variation (CV = 10 percent) was observed due to the manner in which gas mixtures were prepared, but the moisture content did not appear to have any effect on propane trapping efficiency or FID response. Methane was included in the gas mixture which was prepared at 60 percent humidity, and the response obtained was equivalent to that for only propane; indicating that water did not cause increased retention of methane. No significant reduction in flow rate through the cryogenic trap was observed when samples containing high moisture content were analyzed, demonstrating that clogging was not a problem. In some cases of high moisture content a second peak was observed to elute from the cryogenic trap approximately one minute after the hydrocarbon elution zone. This was attributed to collection of polar material in the trap and was not included in peak summation. It was concluded from these studies that water had no significant effect on the analytical method and no steps were included for the removal of water.

Detection Limit

The minimum detectable quantity (MDQ) of nonmethane hydrocarbon was 4×10^{-10} moles - C, which corresponded to approximately 6 ng of ethane or

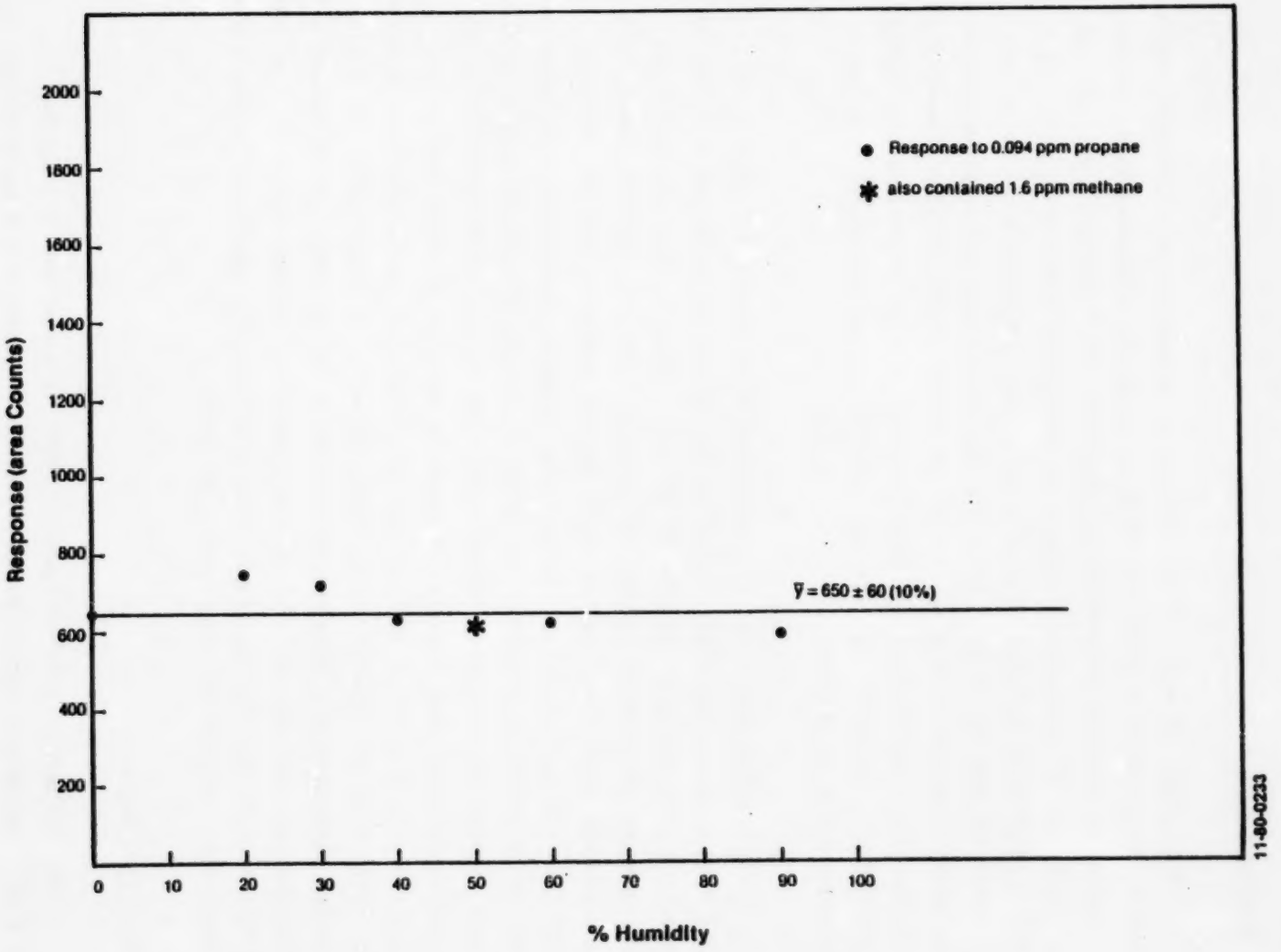


Figure 4. Effect of Water on Response to Propane and Methane.

propane. When using a 500 mL sample, the detection limit was 0.018 ppmv-C (μL-C/L) or 0.006 ppmv-propane. Nonlinearity was less than 10 percent at this level. The detection limit obtained was below the 0.05 ppmv-C level quoted in the QC/QA document (4). The increase in sensitivity was beneficial for accurate analysis of system blanks and ultrapure air.

Reproducibility and Linearity

Reproducibility on standard gas mixtures was generally within 3 percent (CV) in the 0.1 to 1.0 ppmv-C range. Reproducibility on ambient samples will be discussed with the data interpretation. Calibration was highly linear providing correlation coefficients greater than 0.99. This will also be discussed further in the Quality Control/Quality Assurance section.

Typical Hydrocarbon Responses

Typical response of the analytical system to hydrocarbon species are illustrated in Figure 5. An initial noise spike was observed when liquid oxygen was removed from the hydrocarbon trap. Peak integration was initiated immediately following this spike. The propane standard produced a sharp, rapid response (Figure 5-A). When a mixture of C_1-C_{12} n-alkanes was analyzed, a similar but more broad response was observed (Figure 5-D). Ambient samples collected near Nashville and Louisville usually produced several peaks (Figures 5-B and 5-C). With the present analytical system individual peaks were not reproducible, although total peak areas were reproducible.

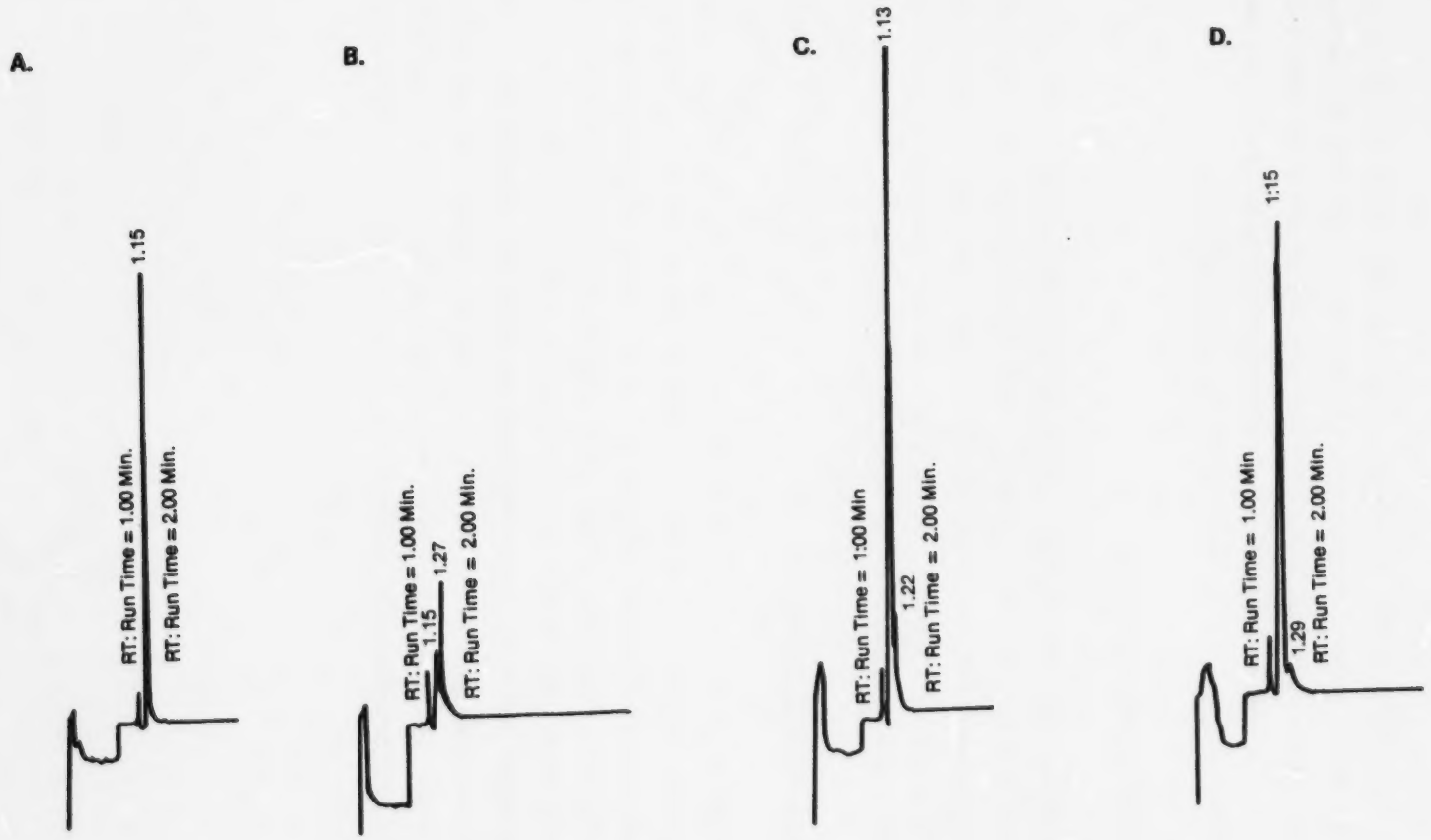


Figure 5. Sample Chromatograms - 5-A. Propane 0.282 ppmv-C, 5-B. Nashville Sample Collected 9/27/80, 0.15 ppmv-C, 5-C. Louisville Sample Collected 9/28/80, 0.422 ppmv-C, 5-D. C_2-C_{12} n-Alkane Mixture.

SECTION 4

SAMPLING SYSTEM

The sampling system was set up as recommended in "Guidance for the Collection and Use of Ambient Hydrocarbon Species Data in Development of Ozone Control Strategies" (2), except for certain modifications which were required during the course of this work. Sampling consisted of collection of three-hour integrated air samples in Tedlar bags and transferring the samples to stainless steel canisters for transport and analysis.

Description

A schematic diagram of the sampling system is presented in Figure 6. A seven-micron stainless steel filter was used as the sampling probe to remove particulate material. Rain water was prevented from entering the system by a cone shaped aluminum shield which was formed around the filter. The sampling probe was connected to the pump by 3 m of 1/4 in. o.d. stainless steel tubing. Air flow through the system was effected with a Metal Bellows model MB-151 pump. Since this pump produced an unrestricted flow of approximately 25 L/min and a flow of only 250-350 mL/min was required to collect three-hour integrated samples, the output of the pump was split so that only a fraction of the flow entered the collection bag. This was accomplished by splitting the pump output with a stainless steel tee and two flow restrictors. The flow restrictor between the tee and collection bag consisted of a measured length of 1/16 in. o.d. x 0.01 in. i.d. stainless steel tubing. A stainless steel fine metering valve (Nupro® no. SS-2MG) was used as the second flow restrictor. Air flow through this restrictor was vented to the atmosphere. The two restrictors were set so that the flow entering the sampling bag was between 250 and 350 mL/min and a flow of 1.5 to 3.5 L/min

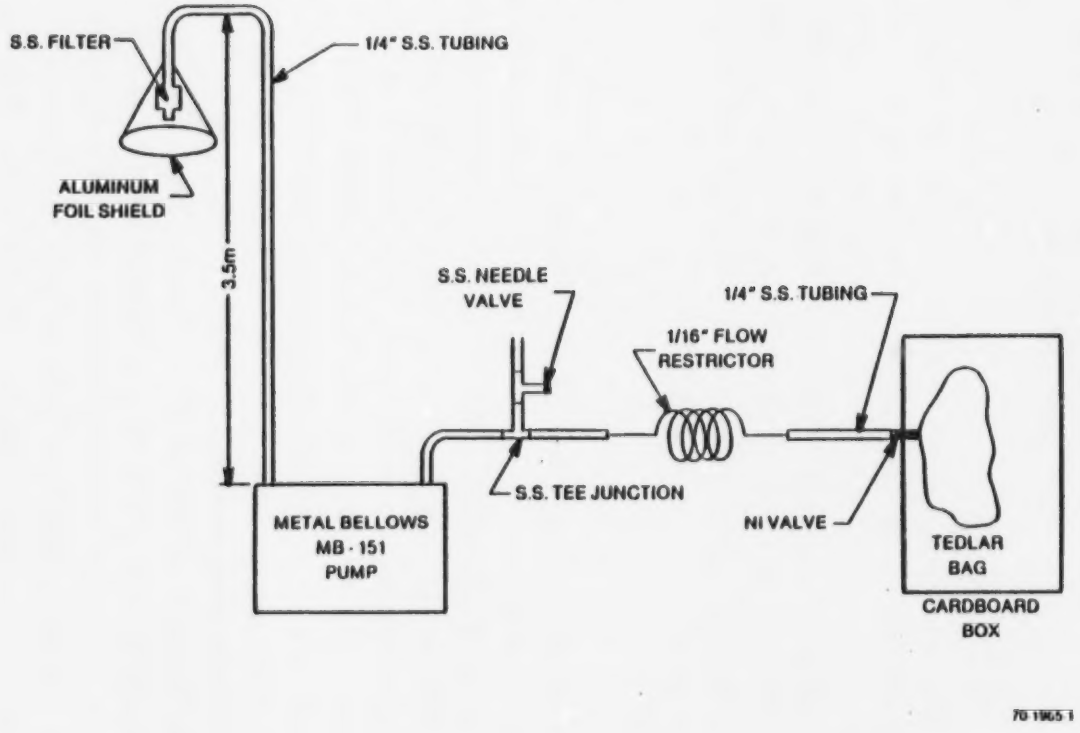


Figure 6. Ambient Air Sampling Train.

was exhausted to the atmosphere through the fine metering valve. Although a range of flow rates was used for the two sites, the flow was set at a constant rate at the beginning of each sampling period and this did not vary by more than 15 percent during the 3-hour period.

Samples were collected in 70 L Tedlar bags (30 in. x 30 in. x 0.002 in.) which were fitted with Roberts 30A-C nickel plated valves. The valves could be rotated to open or shut off flow to the bags. The bags were enclosed in cardboard boxes during sampling to shield them from light. When sampling was completed, the collected air was pumped from the Tedlar bag into 2.8 L stainless steel canisters, which were pressurized to approximately 30 psi. The canisters used were obtained from D & S Instruments, Pullman, Washington, and had been electropolished by the SUMMA® process.

Tedlar Bags

Tedlar bags were tested by filling them with ultrapure air and measuring the total nonmethane hydrocarbon levels after three hours. A 3-hour value of less than 0.05 ppmv-C was considered acceptable. It was found that when initially purchased, the bags required a minimum of five purges with ultrapure air before the acceptable level was reached. It was also found that these bags should be completely protected from exposure to sunlight and heat. Tedlar bags which were exposed directly or indirectly (through a dark colored garbage bag) to sunlight emitted high levels of nonmethane hydrocarbons. This emission continued for several weeks after exposure even though bags were stored in the dark. During this project, efforts were made to always keep the Tedlar bags cool and in the dark.

Stainless Steel Canisters

Stainless steel canisters were cleaned by heating to 100°C for 15 minutes with a slow flow (20-50 mL/min) of ultrapure air passing through them. Following this, the canisters were cooled, pressurized to 30 psi, and

after several hours the air within was analyzed. A nonmethane hydrocarbon level of less than 0.05 ppmv-C was considered acceptable for canisters. It was found that canisters were much easier to clean and keep clean than the bags. All canisters were pressurized and analyzed when initially obtained, although no contamination was found when canisters were purchased from the aforementioned manufacturer. The cleanup procedure for canisters was repeated after each use.

Pumping System

The pump was tested for contamination by pumping ultrapure air into a precleaned Tedlar bag for three hours. Following this, air from the bag was pressurized into a precleaned stainless steel canister and analyzed. This technique actually measured the total contamination produced by the pump, bag, canister, and sample transfer. A level of 0.1 ppmv-C was considered acceptable as a three-hour blank value for the entire sampling system.

It was found that the pumping system can be the major contributor to hydrocarbon contamination of the sample and that it also may be the most difficult component of the sampling system to clean and keep clean. Initially, the pumping system was set up as recommended by EPA (2). It is recommended in this document that a flow restrictor be used to reduce the output of the sampling pump from 25 L/min to the required 300 mL/min. When the sampling system was constructed in this manner, acceptable blank values were obtained for 30 minutes of operation. However, when the system was operated for 3 hours, the pump became hot and nonmethane hydrocarbon levels from 0.1 to 0.5 ppmv-C were observed. Excessive heating of the pump is not desirable since it could cause increased emission of hydrocarbon residues in the pump and the warm air produced could cause increased leaching of contaminants from bag surfaces.

It was found that the pumps produced the least heat when a flow between 1.5 and 10 L/min was maintained. This was accomplished in the sampling system by using two flow restrictors and splitting the pump output. Flow through the sampling restrictor was approximately 300 mL/min and flow through the exhaust restrictor was approximately 2.5 L/min. This was most easily accomplished using a needle valve as the exhaust restrictor. In addition to the pump operating at a cooler temperature, only 10 percent of contaminants produced by the pump passed into the Tedlar bag when the sampling system was set up in this manner.

Sampling Procedure

Prior to initiation of sample collection the sampling system was purged with ambient air for 30 minutes. This allowed the removal of material which may have condensed in the sampling system while not in use and allowed the pump and all transfer lines to reach an equilibrium temperature. During this time the bag (or bags) to be used on that day were purged with ultrapure or ambient air. The pump was disconnected momentarily to empty the bag. After the pumping system and bag had been purged, the exhaust and sampling flows were set at their respective levels and the Tedlar bag was placed in a cardboard box. Sampling was initiated daily at 6:00 am and continued for a 3-hour period.

When sample collection was completed, the bag was disconnected from the sampling line and closed by means of the nickel valve. The pump was allowed to continue running until the sampling and exhaust flows were measured. Once this was accomplished the exhaust restrictor was opened completely and the sampling line was purged of any water which had collected in it. Moisture was observed in the needle valve used for the exhaust restrictor when samples were collected during conditions of high humidity or precipitation. Moisture was not observed in the 1/16 in. restrictor leading to the collection bag or in the collection valve. The Tedlar bag containing the three-hour integrated sample was then connected to the pump input and the sample

was pumped into an evacuated stainless steel canister. This canister was evacuated and filled two more times to assure a representative sample. On the final filling, the canister was pressurized to approximately 30 psi and the sample number and pressure was recorded.

Normally, two canisters were purged and filled from the Tedlar bag sample collected on a given day. As a quality assurance measure, samples were collected on several days in duplicate Tedlar bags. This was accomplished by decreasing the length of sample restriction tubing to double the sample flow and splitting the flow into two Tedlar bags. In this case only one canister was filled from each bag.

When sample collection was completed and the stainless steel canisters filled, the remainder of the sample was pumped from the Tedlar bag and the bag flushed twice with ultrapure air. Filters were backflushed several times with high pressure surges of ultrapure air, then with a slow flow of ultrapure air for 10 minutes. Four filters were used at each site. All sampling lines were then reconnected with the appropriate flow rates set and ultrapure air was pumped through the sampling system for 20 minutes after which the sampling input and outputs were sealed.

Blanks were collected by pumping ultrapure air through the entire sampling system and into a Tedlar bag for 3 hours. The air in the Tedlar bag was transferred to a single stainless steel cylinder for transport and analysis.

Since the ultrapure air used contained detectable quantities of non-methane hydrocarbons, samples of this were also collected in stainless steel canisters and shipped to the laboratory for analysis.

SECTION 5

SAMPLE COLLECTION

The criteria used for site selection were those recommended for NMHC collection in EPA reports (2,3). EPA stipulated that the collection sites should be two existing ambient air monitoring laboratories in Louisville and Nashville. Within this restriction sites were chosen to collect samples which were representative of the average air composition in that area.

Sample collection at the Louisville site was initiated on September 16, 1980, and completed on September 30, 1980. Sample collection at the Nashville site was initiated on September 19, 1980, and completed on October 2, 1980. All samples and accompanying data sheets were shipped directly to Radian's Austin laboratory via air express.

Louisville Site

The ambient air sampling site for Louisville was near a state-owned monitoring station located approximately 20 km south of the city. The exact location of the sampling probe was chosen to be approximately equidistant from surrounding gas stations, a school bus parking lot, and a highway. A drawing of the site is presented in Figure 7. The site was also chosen upwind of the monitoring station (by wind records of the previous year) to avoid possible contamination from ozone monitors in the trailer. The sampling probe was located 4.5 meters above ground level and 3 meters above the support platform.

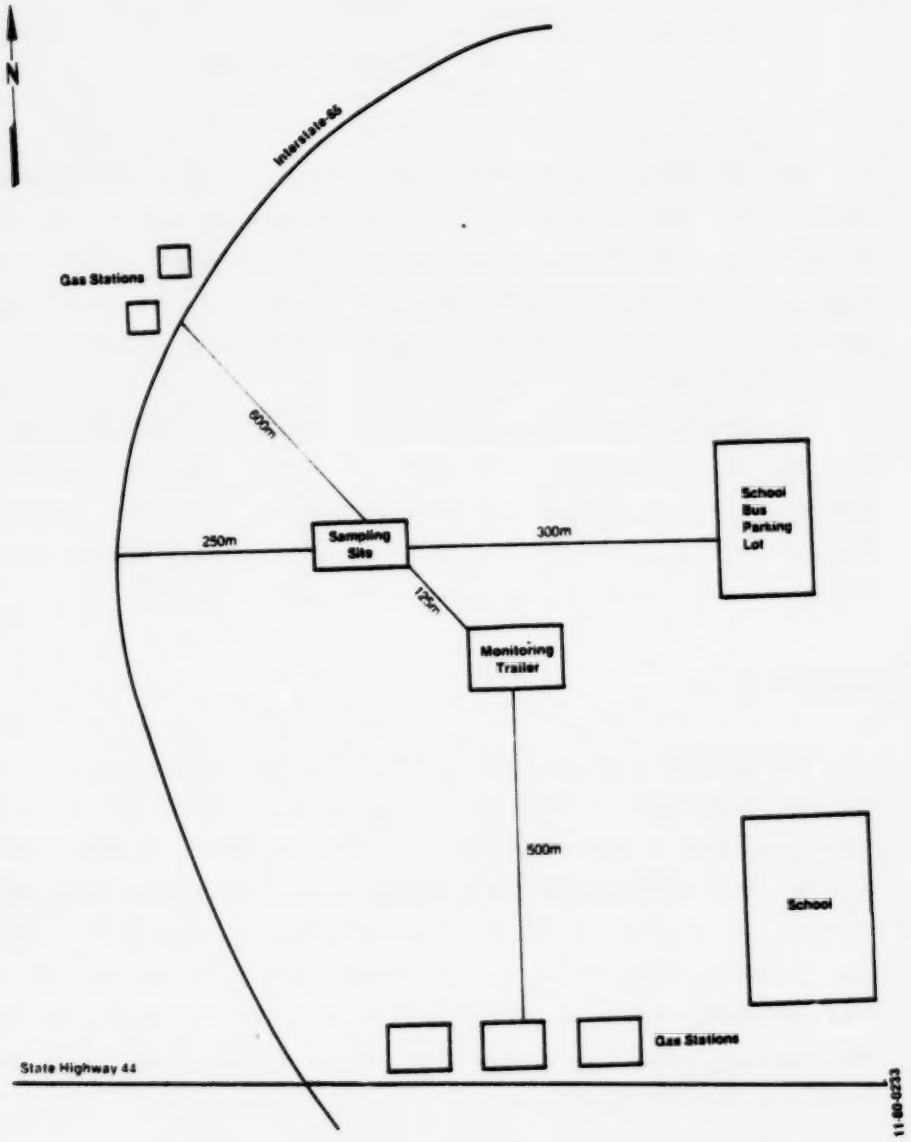


Figure 7. Louisville Sampling Site in Shepardsville, KY - Approximate Layout.

Approximately 15 school buses were situated 300 meters east of the sampling site. These were started at 7:00 am five mornings a week and allowed to warm up for 20 minutes. Two gas stations were located 600 meters northwest of the sampling site and 3 more were located 500 meters south of the sampling site. No tank truck off-loading was observed during the 6:00 am - 9:00 am sampling periods. An interstate highway (I-65) ran north to south about 250 meters west of the site. Travel on the highway from 6:00 am - 9:00 am was approximately 300 cars. A school was located southeast of the site.

Weather data during sampling were obtained from the Louisville airport which was about 20 km north of the site. In addition, weather data collected at the sampling site were obtained from the Division of Air Pollution Control of the Kentucky Department for Natural Resources and Environmental Protection.

Nashville Site

The ambient air monitoring site for Nashville was on the University of Tennessee Agricultural Testing Facility in Spring Hill, Tennessee; approximately 60 km south of Nashville. The state monitoring station was in a fairly secluded area on the eastern edge of the testing facility. A diagram of the area is presented in Figure 8. One possible source of contamination at this site was the Bull Testing Labs located 50 meters east of the monitoring station. Samples at this site were collected approximately 5.5 meters above ground level and 1.5 meters above the roof of the monitoring trailer. The exhaust from the ozone monitor was vented underneath the trailer. A 10 meter length of polyethlyne tubing was connected to this and was always positioned so that the exhaust was at ground level and downwind of the sampling probe.

Wind direction data were obtained from monitoring equipment operating in the trailer. All other weather data were obtained from the U.S. Weather Service at the Nashville Airport, which was about 70 km northeast of the sampling site.

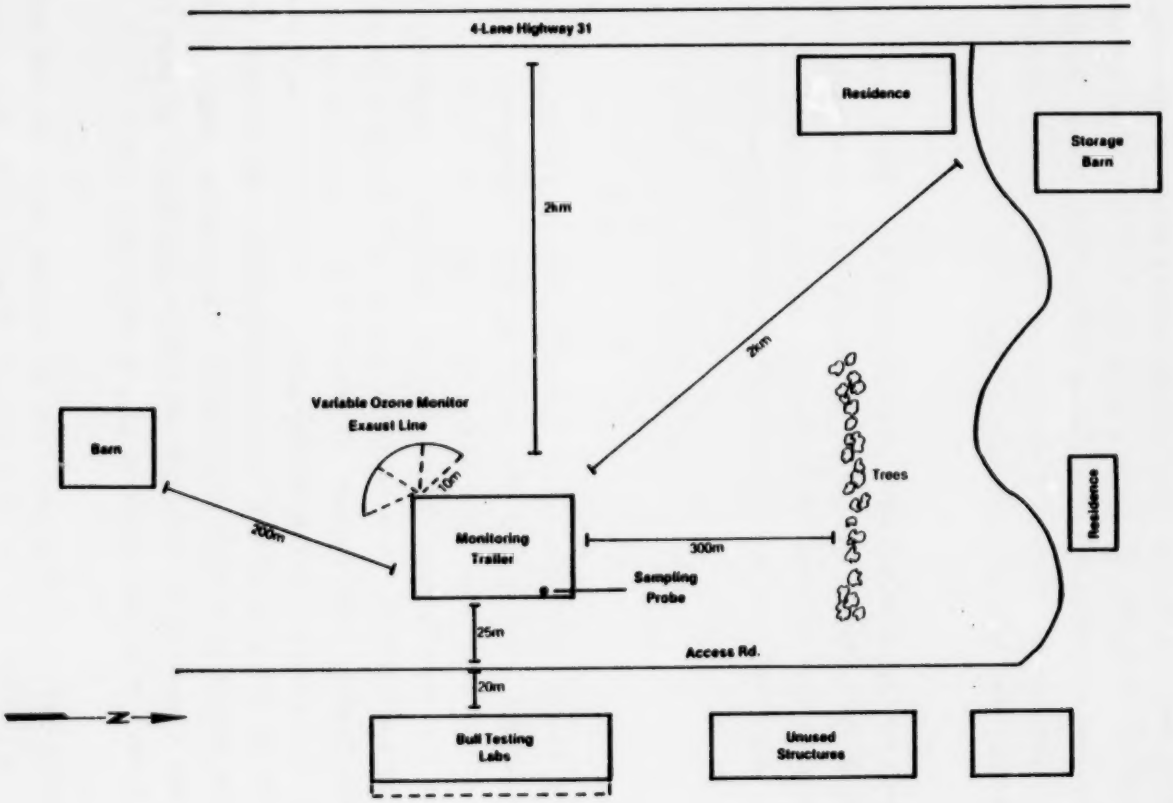


Figure 8. Nashville Sampling Site in Spring Hill TN. Approximate Layout.

Figure 8. Nashville Sampling Site in Spring Hill, TN - Approximate Layout.

SECTION 6

SAMPLE ANALYSIS

When shipments were received in the laboratory, the data sheets were collected and samples logged in. All samples were given a code number which was the only identification provided to the analyst. Prior to analysis the pressure of each canister was checked and recorded.

Each canister was analyzed in duplicate or triplicate providing four to six data measurements per day. Quantitation was based on a linear calibration prepared with a 0.094 ppmv NBS traceable propane standard prior to analysis. Sample volumes were kept at or below 400 mL to assure complete trapping of ethane and ethylene.

SECTION 7

RESULTS

Data were obtained over a 15 day period for Louisville and over a 14 day period for Nashville. All NMHC and weather data will be reported in this section. By means of a thorough QC/QA program, it was possible to assess individual error contributions from various components of the sampling and analytical methods and calculate confidence limits for the NMHC data. All statistical calculations will be discussed in the QC/QA section of this report.

Nonmethane Hydrocarbon Data

The nonmethane hydrocarbon concentrations found in ambient air samples collected near Louisville, Kentucky, are presented in Table 2 and those concentrations found in samples collected near Nashville, Tennessee, are presented in Table 3. NMHC concentrations are reported as ppmv-C (μL-C/L) on a dry air basis. One sample at each site was collected daily (in one or two Tedlar bags) and transferred to two stainless steel canisters. The average NMHC value and analytical variation for each canister are presented in Tables 2 and 3 as well as the daily averages for both canisters. The daily NMHC values were corrected for sampling system contributions at each site. These data, along with confidence limits, are also presented in these tables.

Variability of the duplicate canister samples which were collected daily at each site is illustrated graphically in Figures A-1 and A-2 of Appendix A.

TABLE 2. AMBIENT NONMETHANE HYDROCARBON LEVELS FOUND NEAR LOUISVILLE, KENTUCKY

Date	Sample Type[1]	NMHC Concentration[2] (ppmv-C)	Daily Average[3] (ppmv-C)	Corrected Value[4] (ppmv-C)	Confidence Limits[5] (ppmv-C)
9/16	DC	0.380±0.010	0.420±0.057	0.368±0.045	0.278-0.458
		0.461±0.014			
9/17	DC	0.211±0.010	0.198±0.018	0.146±0.028	0.091-0.201
		0.185±0.004			
9/18	DC	0.460±0.017	0.453±0.009	0.404±0.045	0.314-0.494
		0.446±0.017			
9/19	DC	0.308±0.008	0.318±0.014	0.266±0.045	0.176-0.356
		0.328±0.026			
9/20	DC	0.416±0.003	0.416±0.000	0.364±0.045	0.274-0.454
		0.416±0.026			
9/21	DC	0.155±0.013	0.158±0.004	0.106±0.029	0.050-0.162
		0.160±0.023			
9/22	DC	0.189±0.020	0.240±0.073	0.188±0.044	0.099-0.277
		0.292±0.035			
9/23	DC	0.200±0.006	0.180±0.028	0.128±0.028	0.072-0.184
		0.161±0.014			
9/24	DB	0.284±0.024	0.274±0.014	0.222±0.039	0.144-0.300
		0.264±0.006			
9/25	DC	0.262±0.001	0.255±0.010	0.203±0.045	0.113-0.293
		0.248±0.005			
9/26	DB	0.205±0.007	0.204±0.001	0.152±0.039	0.074-0.230
		0.204±0.001			
9/27	DC	1.003±0.024	1.016±0.019	0.964±0.045	0.874-1.054
		1.030±0.088			
9/28	DB	0.422±0.022	0.364±0.083	0.312±0.039	0.234-0.390
		0.305±0.003			
9/29	DC	0.634±0.027	0.644±0.014	0.592±0.045	0.502-0.682
		0.654±0.004			
9/30	DC	0.189±0.019	0.194±0.008	0.142±0.027	0.087-0.197
		0.200±0.022			

[1] DC - duplicate canister sample, DB - duplicate bag sample.

[2] Average nonmethane hydrocarbon value in ppmv-C (by volume) obtained for each canister ± analytical variation (standard deviation).

[3] Daily average for each set of duplicate canisters ± standard deviation.

[4] Daily average minus sampling system blank value ± standard deviation (see Sample and Data Handling in Section 8).

[5] Corrected NMHC value ± 2x standard deviation (95% confidence limits).

TABLE 3. AMBIENT NONMETHANE HYDROCARBON LEVELS FOUND NEAR NASHVILLE, TENNESSEE

Date	Sample Type[1]	NMHC Concentration[2] (ppmv-C)	Daily Average[3] (ppmv-C)	Corrected Value[4] (ppmv-C)	Confidence Limits[5] (ppmv-C)
9/19	DC	0.316±0.009	0.358±0.059	0.336±0.046	0.245-0.427
		0.399±0.047			
9/20	DC	0.118±0.003	0.119±0.001	0.097±0.029	0.040-0.154
		0.120±0.000			
9/21	DC	0.133±0.015	0.139±0.008	0.117±0.028	0.060-0.174
		0.145±0.001			
9/22	DB	0.128±0.011	0.152±0.033	0.130±0.024	0.083-0.177
		0.175±0.027			
9/23	DC	0.094±0.018	0.106±0.017	0.084±0.028	0.027-0.141
		0.118±0.002			
9/24	DC	0.191±0.004	0.186±0.007	0.164±0.029	0.107-0.221
		0.180±0.021			
9/25	DC	0.153±0.010	0.160±0.010	0.138±0.028	0.082-0.194
		0.167±0.020			
9/26	DC	0.090±0.006	0.090±0.000	0.068±0.029	0.011-0.125
		0.090±0.002			
9/27	DB	0.145±0.017	0.138±0.010	0.116±0.024	0.068-0.164
		0.130±0.000			
9/28	DC	0.038±0.001	0.088±0.008	0.066±0.029	0.009-0.123
		0.094±0.003			
9/29	DC	0.106±0.023	0.111±0.007	0.089±0.028	0.032-0.146
		0.116±0.011			
9/30	DC	0.083±0.009	0.082±0.001	0.060±0.029	0.003-0.117
		0.082±0.002			
10/1	DC	0.090±0.012	0.094±0.006	0.072±0.029	0.015-0.129
		0.098±0.006			
10/2	DC	0.110±0.018	0.112±0.002	0.090±0.028	0.336-0.146
		0.113±0.013			

[1] DC - duplicate canister sample, DB - duplicate bag sample.

[2] Average nonmethane hydrocarbon value in ppmv-C (by volume) obtained for each canister ± analytical variation (standard deviation).

[3] Daily average for each set of duplicate canisters ± standard deviation.

[4] Daily average minus sampling system blank value ± standard deviation (see Sample and Data Handling in Section 8).

[5] Corrected NMHC value ± 2x standard deviation (95% confidence limits).

Weather Data

The weather conditions existing during sample collection in Louisville are presented in Table 4 and those existing during sample collection in Nashville are presented in Table 5. With the exception of precipitation, all other data for the Louisville site were obtained from the National Weather Service at the Louisville Airport. For the Nashville site, wind direction and precipitation data were collected on site and all other data were obtained from the National Weather Service at the Nashville Airport. NMHC values for each day are included in these tables for reference.

Wind direction and wind velocity data were collected from the Louisville sampling site by the Division of Air Pollution Control of the Kentucky Department for Natural Resources and Environmental Protection. These data were obtained from this agency and are presented in Appendix A. The wind direction data obtained from the Kentucky Division of Air Pollution Control (KDAPC) were in good agreement with those obtained from the National Weather Service at the Louisville Airport, however, wind speed data obtained from the KDAPC were always less than those obtained from the National Weather Service. These data were used to determine if high NMHC values obtained on certain days were a function of local contributions. Plots of NMHC as a function of wind direction and speed are presented in Appendix A. From the plots for Louisville, KY it appears that the high NMHC values occurred when the wind direction was from the north-northeast (9/27, 9/29, 9/18, 9/20). This tends to implicate the school bus lot as a source of contamination. However, two of these sampling dates (9/27/9/20) fell on weekends when the buses were not in service. Since the sampling site is situated south of the city of Louisville, KY, high NMHC values on days with northerly winds could be a result of city emissions.

TABLE 4. WEATHER CONDITIONS DURING AMBIENT AIR SAMPLING NEAR LOUISVILLE, KENTUCKY

Date	Temperature (°F)	Pressure (in Hg)	Relative Humidity (%)	Wind Speed (mph)	Wind Direction	Precipitation[1]	Corrected NMHC Concentration (ppmv-C)
9/16	60	29.90	92	5	E		0.37
9/17	66	29.82	90	7	SW	R	0.15
9/18	58	29.60	92	6	NE	F	0.40
9/19	58	30.22	94	5	N	F	0.27
9/20	71	30.10	82	7	S		0.36
9/21	78	29.98	80	7	S		0.11
9/22	78	29.96	82	7	S	R	0.19
9/23	65	30.01	86	12	N		0.13
9/24	60	30.04	86	7	NE		0.22
9/25	63	30.00	95	3	S	F	0.20
9/26	54	30.32	72	8	NW		0.15
9/27	51	30.35	78	6	N		0.96
9/28	55	30.20	83	5	NE		0.31
9/29	58	30.10	79	4	NE		0.59
9/30	65	29.97	82	6	E		0.14

[1] R - rain; F - fog or mist

TABLE 5. WEATHER CONDITIONS DURING AMBIENT AIR SAMPLING NEAR NASHVILLE, TENNESSEE

Date	Temperature (°F)	Pressure (in Hg)	Relative Humidity (%)	Wind Speed (mph)	Wind Direction	Precipitation[1]	Corrected NMHC Concentration (ppmv-C)
9/19	59	29.53	--	2	NW		0.34
9/20	73	--	--	2	S	R	0.10
9/21	72	--	--	3	SE	F	0.12
9/22	77	30.01	82	3	SE		0.13
9/23	70	29.38	97	8	NE		0.08
9/24	67	29.37	97	3	N	F	0.16
9/25	68	29.35	100	5	NW	F	0.14
9/26	57	29.64	78	8	N		0.07
9/27	53	30.30	83	6	N		0.12
9/28	58	30.18	87	3	E	R	0.07
9/29	63	30.05	90	7	NE	R	0.09
9/30	62	29.93	97	5	NE	R	0.06
10/1	59	29.93	100	4	NW	F	0.07
10/2	67	29.87	84	10	NW	F	0.09

[1] R - rain; F - fog or mist

SECTION 8

QUALITY CONTROL/QUALITY ASSURANCE

The QC/QA program was designed to ensure the reliability of NMHC data collected for this project (4). Discussion of this program will be divided into those aspects dealing with initial project preparation, sample collection, sample analysis, and data handling.

Initial Project Preparation

Prior to initiation of data collection, all analytical and sampling techniques were evaluated to assure accuracy and reliability of the data.

Analytical Technique

The following aspects of the analytical technique were specified in the QC/QA document and will be discussed here.

System Blank

A system blank was run daily prior to sample analysis. The results of this analysis was used as the zero hydrocarbon level in the calibration for that day. A 500 mL volume of ultrapure nitrogen was passed through all carrier lines and analyzed as a sample. If any response above the detection limit (0.02 ppmv-C) was observed, the system was heated to 130°C and purged. Ultrapure nitrogen was used instead of ultrapure air (as recommended in the QC/QA document) since the UP air contained detectable quantities of nonmethane hydrocarbons which hinderd recognition of the source of low levels of NMHC contamination.

Detection Limit

The lowest quantity of nonmethane carbon which could be reliably detected was 4×10^{-10} moles-C. This was determined using a mixture of ethane in air, since the trapping efficiency for this compound was less than that for other hydrocarbons of interest. The detection limit was defined as that quantity of ethane which produced an area count over 50, which was the level set for noise rejection. This corresponds to a detection limit of 0.018 ppmv-C when using a 500 mL sample. Since it was demonstrated that ethane losses occur above 400 mL, the detection limit for this sample size (0.025 ppmv-C) should be quoted for ambient samples.

Precision

Reproducibility on standard gas samples of ethane or propane was 3 percent or better in the concentration range from 0.1 to 1.0 ppmv-C. Reproducibility of duplicate ambient samples ranged from 0 to 21 percent (CV) with a mean value of 6 percent. Using variance component analysis (see Sample and Data Handling in this section) the mean analytical standard deviation for ambient samples below 0.2 ppmv-C was 0.017 ppmv-C (<22 percent) and that for ambient samples above 0.2 ppmv-C was 0.026 ppmv-C (<13 percent). Precision was much better than the 25 percent limit (at 0.4 ppmv-C) which was initially stated in the QC/QA document.

Linearity

The analytical system was calibrated before and after each set of sample analyses. Calibrations were prepared in the range of 0.03 to 0.3 ppmv-C assuming a 500 mL sample size. Fifty-nine calibrations, each consisting of at least four points, were prepared during the course of this study. Of these, only two gave a correlation coefficient less than 0.99. The analytical system was purged and recalibrated on these occasions. The average correlation coefficient for all calibrations was 0.997.

Sampling Methods

Two types of sample containers were used in this project: stainless steel canisters and Tedlar bags. These containers were cleaned according to EPA recommended procedures (2). Each container was tested by filling it with ultrapure air which was analyzed after three hours. All containers tested below 0.05 ppmv-C before being used in the field.

A variety of sample types were collected to comply with the Quality Control/Quality Assurance plan. Ambient samples were collected either in a single Tedlar bag and transferred to two stainless steel canisters, or were collected in two Tedlar bags, each being transferred to a single canister. In addition, sampling blanks were collected to ascertain the amount of contamination contributed by the sampling system, and the concentration of nonmethane hydrocarbons in the ultrapure air used. Quality control samples were prepared in the laboratory and shipped to the field where the pressure was checked, then returned to the laboratory for analysis.

An inventory of QC/QA samples collected in Louisville is presented in Table 6 and for Nashville in Table 7. Five types of QC/QA samples were used in order to determine error contributions from each component of the sampling technique. All canisters were analyzed in duplicate or triplicate instead of the initial 50 percent frequency for duplicate analyses.

During the sampling procedure, air flow through the sampling system and stainless steel canister pressure were monitored. Sampling flows did not vary by more than 15 percent during any 3-hour sampling period. Also, no significant losses of samples during shipment were observed.

TABLE 6. QC/QA SAMPLING MATRIX FOR LOUISVILLE, KENTUCKY

Date	Sample Type					
	Duplicate Canisters	Duplicate Bags	Replicate Analyses (per day)	Sampling System Blank	Ultrapure Air Blank	Quality Control Standards
9/10					1	
9/11						1
9/12						1
9/16	2*		4	1		
9/17	2		5			
9/18	2		4			
9/19	2		4	1		
9/20	2		4			
9/21	2		4			
9/22	2		6	1		
9/23	2		4			
9/24		2	4			
9/25	2		4			
9/26		2	4			
9/27	2		4			
9/28		2	4			2
9/29	2		4	1		
9/30	2		6			

*Number of S.S. canisters used to collect sample

TABLE 7. QC/QA SAMPLING MATRIX FOR NASHVILLE, TENNESSEE

Date	Sample Type					
	Duplicate Canisters	Duplicate Bags	Replicate Analyses (per day)	Sampling System Blank	Ultrapure Air Blank	Quality Control Standards
9/19	2*		4			
9/20	2		4			
9/21	2		5			
9/22		2	5		1	
9/23	2		5			
9/24	2		4	1		
9/25	2		6			
9/26	2		4	1		
9/27		2	4			
9/28	2		4			
9/29	2		5			
9/30	2		4			1
10/1	2		4	1	1	1
10/2	2		6			1

*Number of S.S. canisters used to collect sample.

Blanks

It was initally stated in the QC/QA document that the entire sampling system, including containers, should not contribute more than 0.1 ppmv-C NMHC contamination to the samples. This was determined by collecting and analyzing 3-hour sampling blanks with the same procedure which was used for ambient air collection. The NMHC concentrations in sampling system blanks which were collected in Louisville and Nashville are presented in Table 8. Also given in this table are NMHC concentrations for the ultrapure air used in collecting blanks. Since there was an initial concentration of NMHC present in the ultrapure air this value must be subtracted from the NMHC blanks for the sampling system. Of seven blanks collected during this project, only one produced an NMHC concentration above the QC limit; although when the UP-air concentration was subtracted from this value, it also fell within the limit.

The average blank values for Louisville and Nashville were tested and found to be statistically different. Therefore, respective blank values were applied to samples collected at each site.

QC Samples

Data for Quality Control samples which were sent into the field and returned to the laboratory for analysis are presented in Table 9. All QC samples were prepared with NBS traceable propane. Absolute errors ranged from -0.029 to +0.021 ppmv-C while relative errors ranged from 0.5 percent to 16 percent. The amount of time expired between preparation and analysis of a sample did not appear to have a significant effect on sample loss or gain.

TABLE 8. NMHC SAMPLING SYSTEM BLANKS FROM LOUISVILLE AND NASHVILLE

Date	Site	Sample Type[1]	NMHC Concentration[2] (ppmv-C)	Average Site Concentration (ppmv-C)	Net Site Concentration (ppmv-C)
9/16	L	SB	0.094±0.014		
9/19	L	SB	0.128±0.006		
9/22	L	SB	0.088±0.010		
9/29	L	SB	0.062±0.006	0.093±0.027	0.052±0.014
9/10	L	UAB	<0.050		
9/24	N	SB	0.075±0.016		
9/26	N	SB	0.049±0.001		
10/1	N	SB	0.064±0.003	0.063±0.013	0.022±0.015
9/22	N	UAB	0.049±0.009		
10/1	N	UAB	0.033±0.009	0.041±0.011[3]	

[1] SB - Sampling System Blank (3-hr); UAB - Ultrapure Air Blank

[2] Average nonmethane hydrocarbon concentration ± analytical deviation (standard deviation).

[3] This value used for UHP air at both sites

TABLE 9. QUALITY CONTROL SAMPLE DATA

Date[1]	Site	NMHC Concentration Prepared (ppmv-C)	NMHC Concentration Observed (ppmv-C)	Absolute Error (ppmv-C)	Relative Error (%)	Delay[2] (days)
9/11	L	0.244	0.258±0.033	+0.014	5.7	4
9/12	L	0.181	0.152±0.022	-0.029	16.0	4
9/28	L	0.213	0.218±0.006	+0.005	2.3	6
9/28	L	0.215	0.214±0.008	-0.001	0.5	7
9/30	N	0.207	0.221±0.002	+0.014	6.8	6
10/1	N	0.116	0.132±0.012	+0.016	13.8	4
10/2	N	0.141	0.162±0.001	+0.021	14.9	4

[1] Date of sample pressure check in field

[2] Number of days between sample preparation and analysis

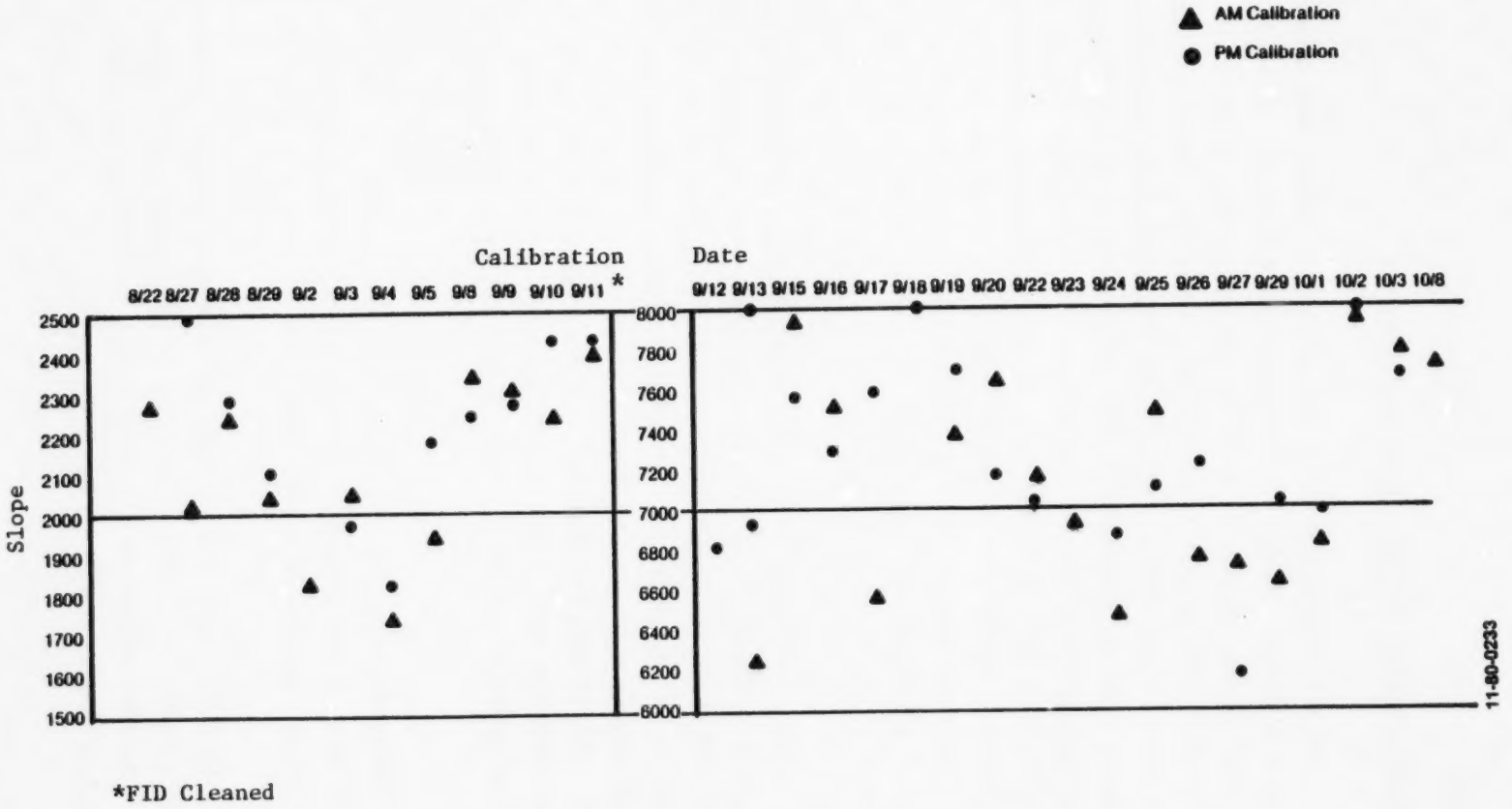
Quality Control During Sample Analysis

The analytical technique was calibrated before and after each set of sample analyses. Each set of calibration points was treated by a least squares linear regression analysis and the slope, y-intercept, correlation coefficient and standard error were calculated. Rejection limits were set for each of these parameters and the analytical instrumentation was checked whenever a parameter fell outside its rejection limit. In addition, quality control charts were kept to monitor day to day variation of the analytical technique. These charts, covering a period from August 22 through October 8, 1980, are presented in Figures 9 through 12. Although sample analysis did not begin until September 17, 1980, calibrations were run previous to this when determining sampling system blanks.

Variation in the calibration slope during the course of this study is shown in Figure 9. During this program, the FID was cleaned and realigned prior to analysis of samples. This resulted in increased sensitivity and a change in the calibration slope. Although this had no effect on the sample data, it did require a new set of units for the quality control chart. After this realignment, the mean value for the slope was 7260 (counts/ppmv-C) with a standard deviation of 575 (8 percent). This type of day-to-day variation is not unusual for a flame ionization detector.

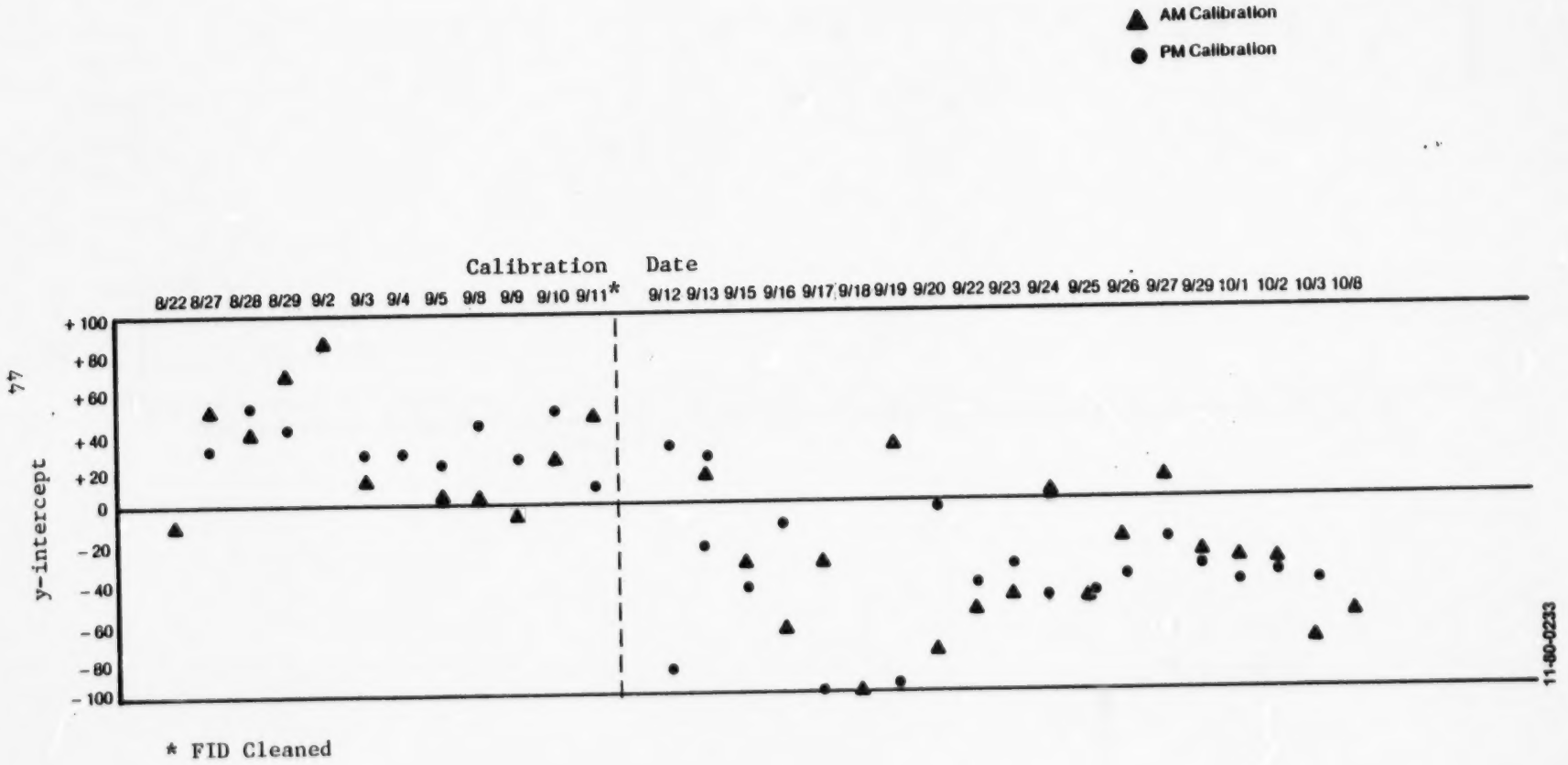
Daily variation in the calibration y-intercept is shown in Figure 10. After the FID realignment, the y-intercept shifted negative. The mean y-intercept during the entire study was -12 with a standard deviation of 46.

The correlation coefficient was used as a measure of system linearity in this study. The daily variation of this parameter is shown in Figure 11. The mean value for all correlation coefficient data was 0.997 with a standard deviation of ±0.003.



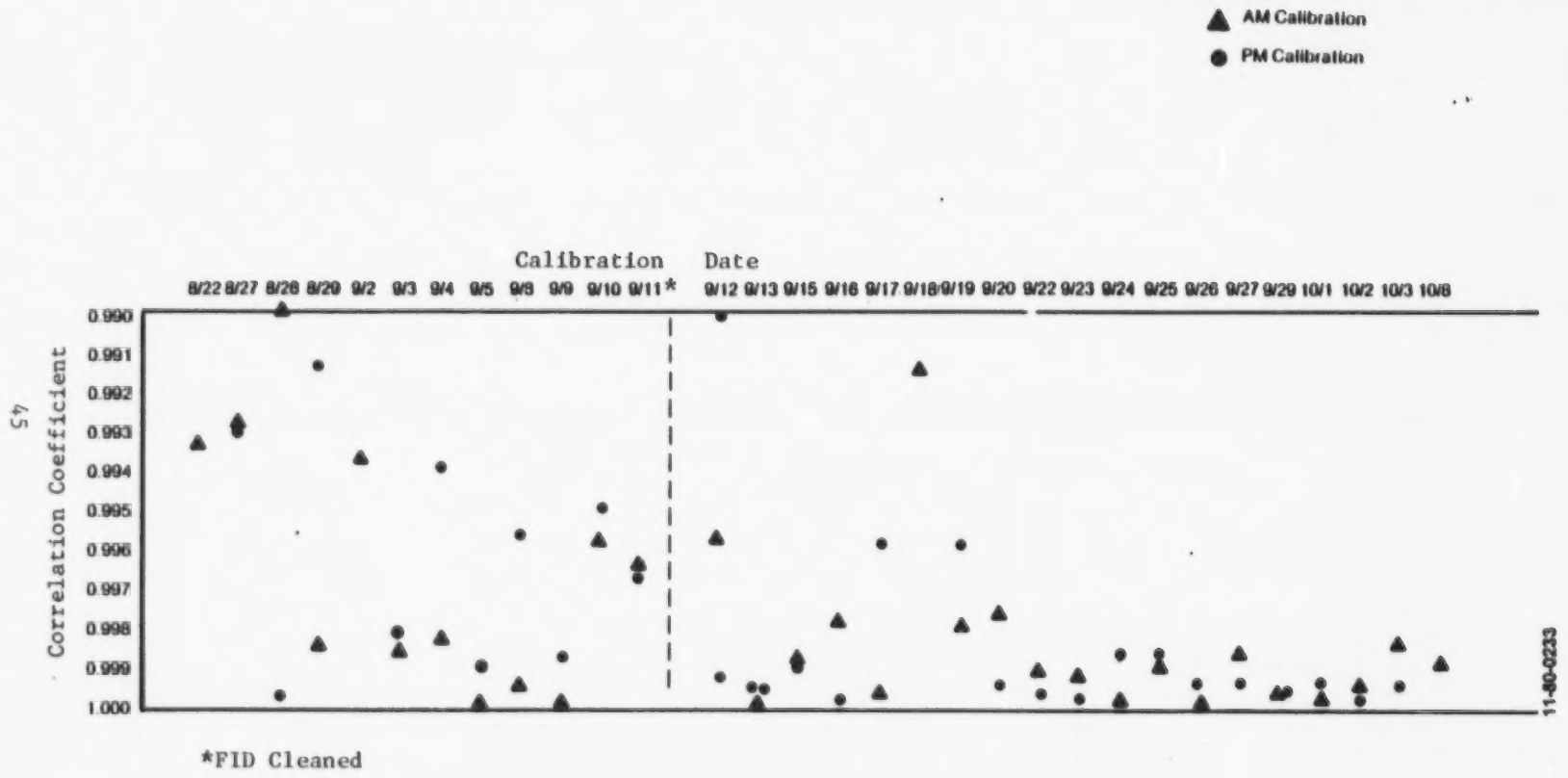
*FID Cleaned

Figure 9. Quality Control Chart for Slope of Calibrations.



* FID Cleaned

Figure 10. Quality Control Chart for y-Intercept of Calibrations.



*FID Cleaned

Figure 11. Quality Control Chart for Correlation Coefficient of Calibrations.

The standard error was used to provide a measure of the scatter of data points around the best-fit line for the calibration. The quality control chart for this parameter is presented in Figure 12. The mean standard error was 57 (±28). The mean relative standard error (obtained by dividing the mean standard error by the mean slope and expressed as a percent) was 0.3 percent.

Sample and Data Handling

All pertinent data concerning sample collection and weather conditions were recorded in permanent notebooks at the sampling sites. These data were also recorded on individual sample log sheets which were shipped along with the samples. When samples were received in the laboratory, the log sheets were collected and each sample was assigned a code number. To avoid experimental bias, the analyst was only provided the sample code number.

Protocol for this type of analysis dictates that the time between sample collection and analysis be seven days or less. In this project every sample was analyzed within three days of collection.

Analysis of the Components of Variance

The NMHC data which were collected are subject to various sources of random variation, including the following:

1) true day-to-day variation in the hydrocarbon levels,
2) variation in the hydrocarbon concentration between Tedlar bags,
3) variance among canisters, and
4) random analytical errors.

Additionally, for each site, a term was subtracted from all hydrocarbon data to account for the system response to ultrapure air (see Section 8.2). This step was performed to remove a possible constant additive bias in the

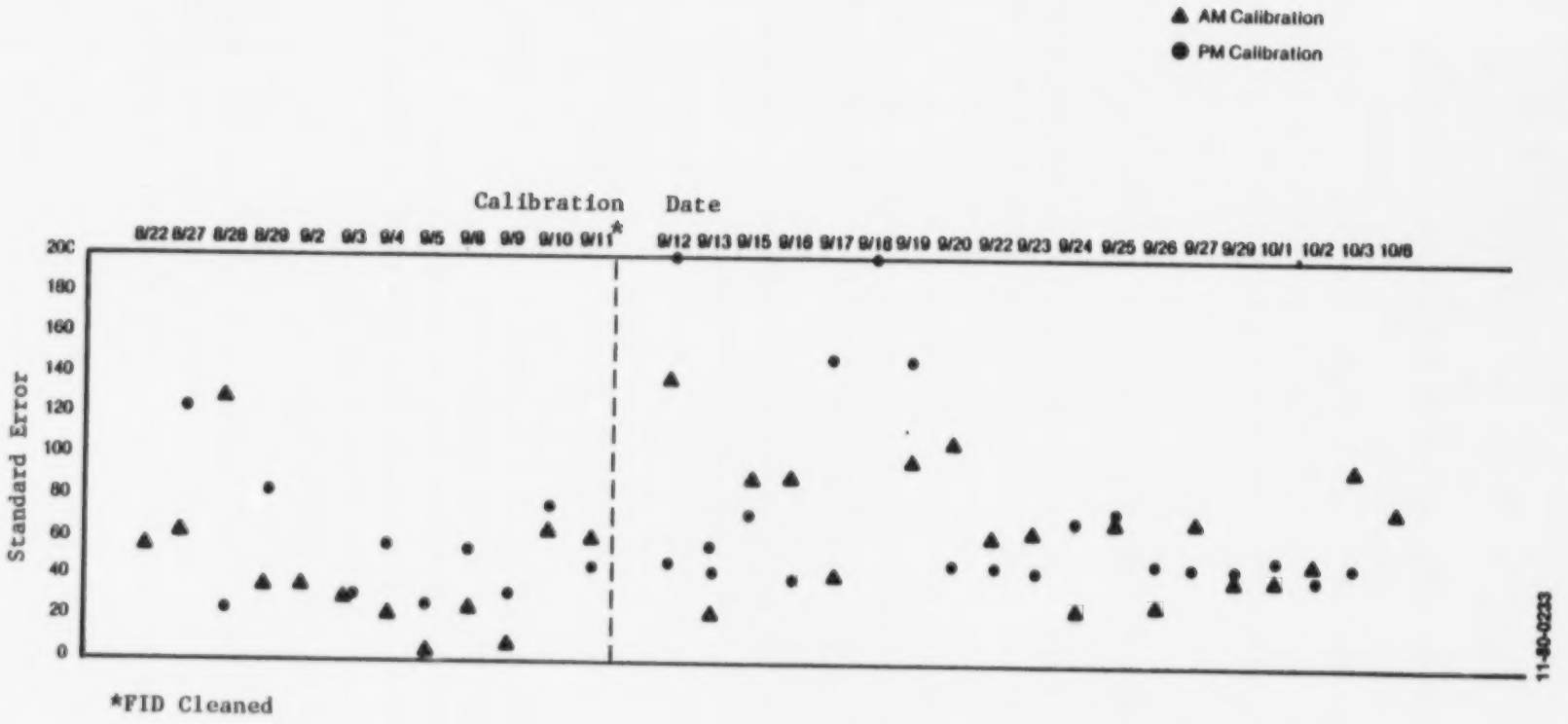


Figure 12. Quality Control Chart for Standard Error of Calibrations.

measurements. The correction terms were derived from finite sets of measurements of blank samples and the NMHC concentrations in the ultrapure air samples and, thus, are subject to random errors. The error in the blank correction term, then, is a fifth source of variance.

It was assumed that a given measured NMHC concentration C can be expressed as follows:

$$C = \mu_{HC} + e_D + e_B + e_C + e_A + e_P$$

where

μ_{HC} = true, long-term average NMHC concentration,
e_D = true variation from the average for this particular sampling day,
e_B = random error associated with all samples drawn from this particular bag,
e_C = random error associated with this canister,
e_A = analytical error, and
e_P = random error associated with the blank correction term.

Thus, an additive random term is associated with each source of variation. It was desired to quantify the variance for each separate error source. The usual equation used to compute the variance δ^2 of a set of n points is:

$$\delta^2 = \frac{\sum_{i=1}^{n} (x_i - \bar{x})^2}{n - 1}$$

where $\bar{x}$ is the sample mean. This equation is not adequate to compute the variances of e_B, e_C, and e_A, however, as is illustrated by the following examples.

Suppose that n samples were collected on a given day from n separate bags. The variance among the n concentrations, then, would not be the variance of e_B, the random error associated with the bags. Differences among the n measurements would also exist due to possible differential

effects of the n cannisters used and due to the n random analytical measurements errors involved. Similarly, concentration measurements of samples in different cannisters from the same bag differ due not only to random canister-to-canister effects (term e_C), but also due to analytical errors.

Thus, isolating the sources of variance cannot be achieved by the straightforward calculation of variances by the equation:

$$\delta^2 = \frac{\sum_{i=1}^{n} (x_i - \bar{x})^2}{n - 1}$$

A statistical technique called variance component analysis (see References 5 and 6), however, can be used to transform estimates of combinations of variances into estimates of variances of individual sources of variation. This technique was used to quantify the error variances due to bag, canister, and analytical effects (e_B, e_C, and e_A). The variance of the error e_p due to the blank correction term was computed separately from the set of blank measurements.

It was suspected that the variances would vary with concentration, and so separate variance component analyses were performed for concentrations less than 0.2 and greater than 0.2 ppmv-C. The size of the data base did not justify further subdivision. The same blank correction term was used for all data for a given site, and so the variance of this term was not separated by concentration.

The variances and standard deviations (the square root of the variances) for the different sources of random error are presented in Table 10. The largest variances were associated with the canisters, followed by the bag variances, followed by the analytical variances. The random errors of the blank corrections have smaller variances than any of the above. All of the error components have standard deviations less than or equal to 0.0620 ppmv-C.

TABLE 10. VARIANCE COMPONENTS FOR SOURCE CONTRIBUTIONS

Source	Site	NMHC Conc. (ppmv-C)	Variance Component	Standard Deviation (ppmv-C)
Analytical	N, L	<0.2	0.000291	0.0171
Analytical	N, L	>0.2	0.000698	0.0264
Tedlar Bags	N, L	<0.2	0.000495	0.0222
Tedlar Bags	N, L	>0.2	0.00104	0.0322
Canisters	N, L	<0.2	0.00384	0.0620
Canisters	N, L	>0.2	0.00125	0.0354
Blank	N	All	0.00023	0.015
Blank	L	All	0.00019	0.014

The variance components presented in Table 10 were used to compute the standard errors of the average of the NMHC measurements for each day for each site. The standard error δ_e for a given day was calculated as follows:

$$\delta_e = \left[\frac{\delta_B^2}{n_{SB}} + \frac{\delta_A^2}{n_A} + \frac{\delta_C^2}{2} + \delta_P^2 \right]^{1/2}$$

Where

δ_B^2 = variance component for bags,

n_{SB} = number of bags used on that day (one or two)

δ_A^2 = analytical variance component,

n_A = total number of analytical determinations performed for both air samples (four, five or six)

δ_C^2 = variance component for canisters (two canisters were used each day), and

δ_P^2 = variance of the error is the blank correction term

The different variance components are divided by the appropriate factors to account for reductions in the variances due to averaging effects. To illustrate, averaging replicate analyses of the air sample from a single canister reduces the analytical uncertainty but does not affect the additive random effects due to canisters or bags. Since only one canister and only one bag are involved, no "averaging" of the random bag-or-canister-associated errors is achieved. The different divisions of the variance components are designed to account for this kind of effect. Actually, two canisters were used on each day and two bags were also used on some days.

Confidence limits for each day's average NMHC concentration were calculated as ± twice the standard error. These values were presented in Tables 2 and 3.

Weather and Data Correlations

Statistical tests were run to determine if any correlations existed between NMHC levels and weather conditions or data. These were performed to identify any systematic errors associated with the data. Since this study was intended to determine NMHC levels upwind of the cities of interest, tests were run to determine if wind direction or wind speed impacted the data. Plots were also prepared to determine if NMHC concentrations varied during different days of the week, which might suggest local influences. Correlation plots were also prepared to determine if other weather conditions could impact atmospheric NMHC concentrations. These studies provide further insight on the validity of the analytical data or on any factors which might directly affect atmospheric NMHC levels.

Plots of NMHC concentration as a function of weather conditions and data are presented in Appendix A. Data points from duplicate samples were treated independently in these plots.

The correlation coefficients indicating possible relationships between NMHC concentrations and temperature, humidity, wind speed and pressure are presented in Appendix A. The correlation coefficient is a measure of the strength of the linear relationship between two variables; its square is interpretable as the fraction of the variance in either variable that can be explained or predicted in terms of the other. In Louisville, slight negative correlations were observed between NMHC concentration and temperature and wind speed; while for Nashville slight negative correlations were observed between NMHC concentration and wind speed and pressure. These observations should be viewed with discrimination since a limited number of data points were available for the study. Although correlation coefficients could not be calculated for wind direction data (non-numerical variable), plots of wind direction and NMHC concentrations for each site were prepared and are presented in Appendix A. With the number of data

points available it is not possible to recognize (from these plots) any relationship between wind direction and NMHC concentrations.

REFERENCES

1. State Implementation Plans: Approval of 1982 Ozone and Carbon Monoxide Plan Revisions for Areas Needing an Attainment Date Extension. Federal Register. 45(191): 64856-64861, 1980.

2. Singh, H.B. Guidance for the Collection and Use of Ambient Hydrocarbon Species Data in Development of Ozone Control Strategies. EPA-450/4-80-008, U.S. Environmental Protection Agency, Research Triangle Park, NC, 1980.

3. Guidance for Collection of Ambient Non-Methane Organic Compound (NMOC) Data for Use in 1982 Ozone SIP Development, and Network Design and Siting Criteria for the NMOC and NO_x Monitors. EPA-450/4-80-008, U.S. Environmental Protection Agency, Research Triangle Park, NC 1980.

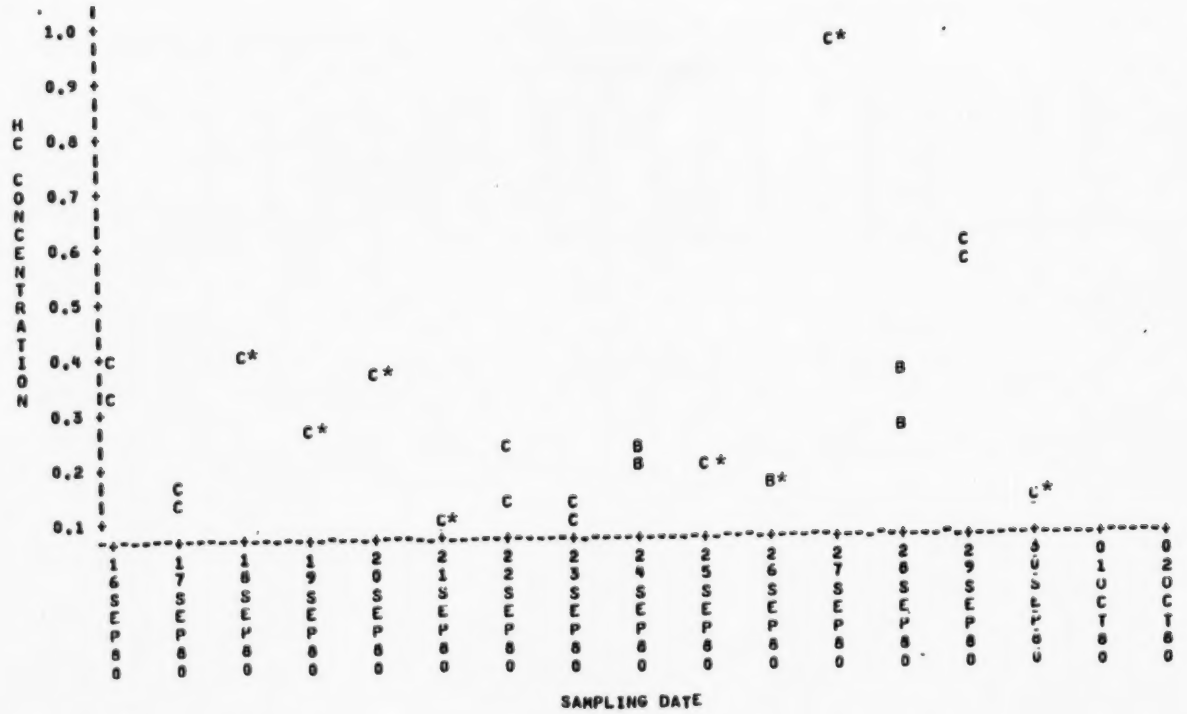
4. Lee, K.W., QC/QA Document for Collection and Analysis of Nonmethane Hydrocarbon Data From Upwind Ozone Monitoring Sites. DCN 80-240-016-01-03. Radian Corporation, Austin TX, 1980.

5. SAS Users Guide, 1979 Edition. SAS Institute, Inc., P.O. Box 10066, Raleigh, NC, 1979. SAS Nested Procedure, page 313.

6. Searle, S.R., Linear Models, John Wiley and Sons, Inc., New York, 1971.

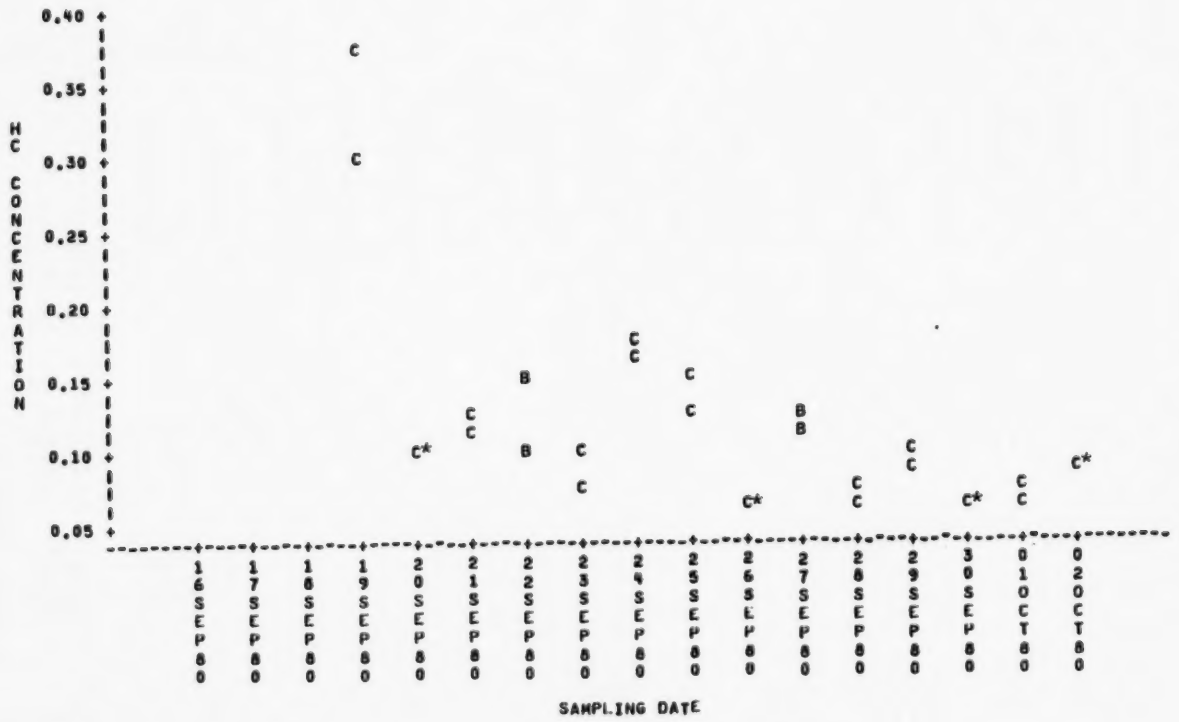
APPENDIX A

NMHC: WEATHER CORRELATION PLOTS



NOTE: *Data points coincided.

Figure A-1. NMHC Concentration Plotted as a Function of Sampling Date: Louisville Site
B - Duplicate Bag Sample, C- Single Bag/Duplicate Canister Sample,
* - Data Points Coincided for That Day.



NOTE: *Data points coincided.

Figure A-2. NMHC Concentration Plotted as a Function of Sampling Date: Nashville Site
B - Duplicate Bag Sample, C - Single Bag/Duplicate Canister Sample,
* - Data Points Coincided for That Day.

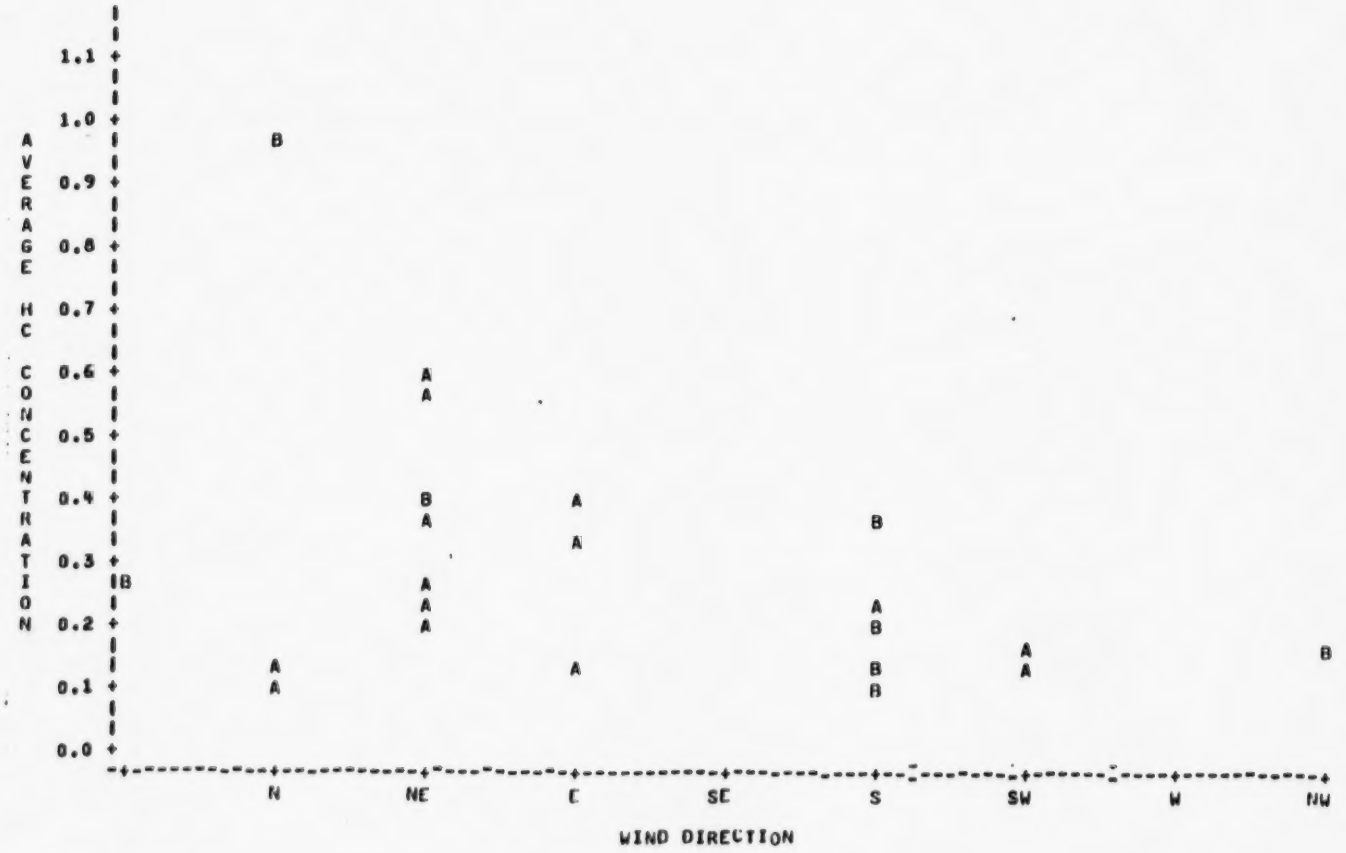


Figure A-3. NMHC Concentration Plotted as a Function of Wind Direction: Louisville Site. A = 1 Observation, B = 2 Observations.

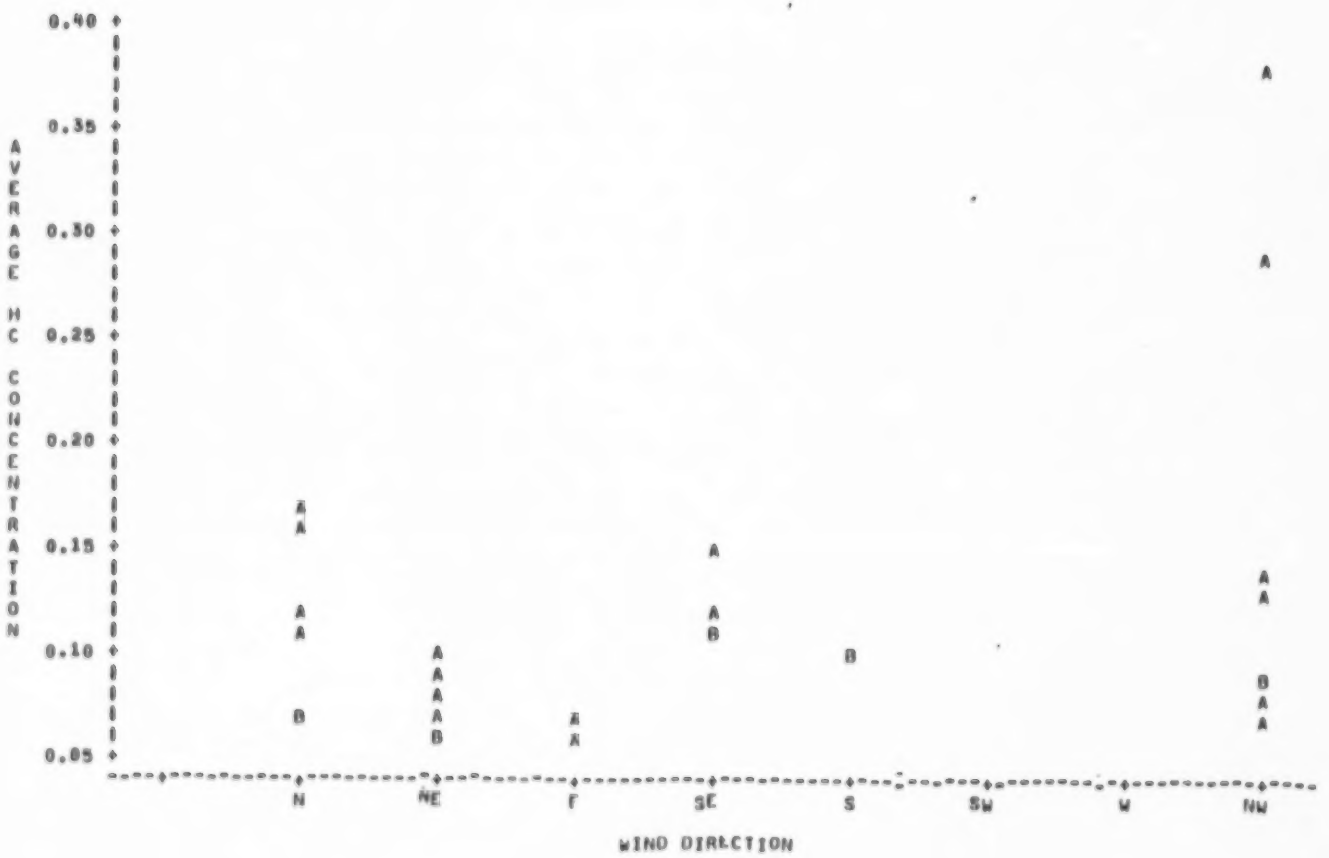


Figure A-4. NMHC Concentration Plotted as a Function of Wind Direction: Nashville Site. A = 1 Observation, B = 2 Observations.

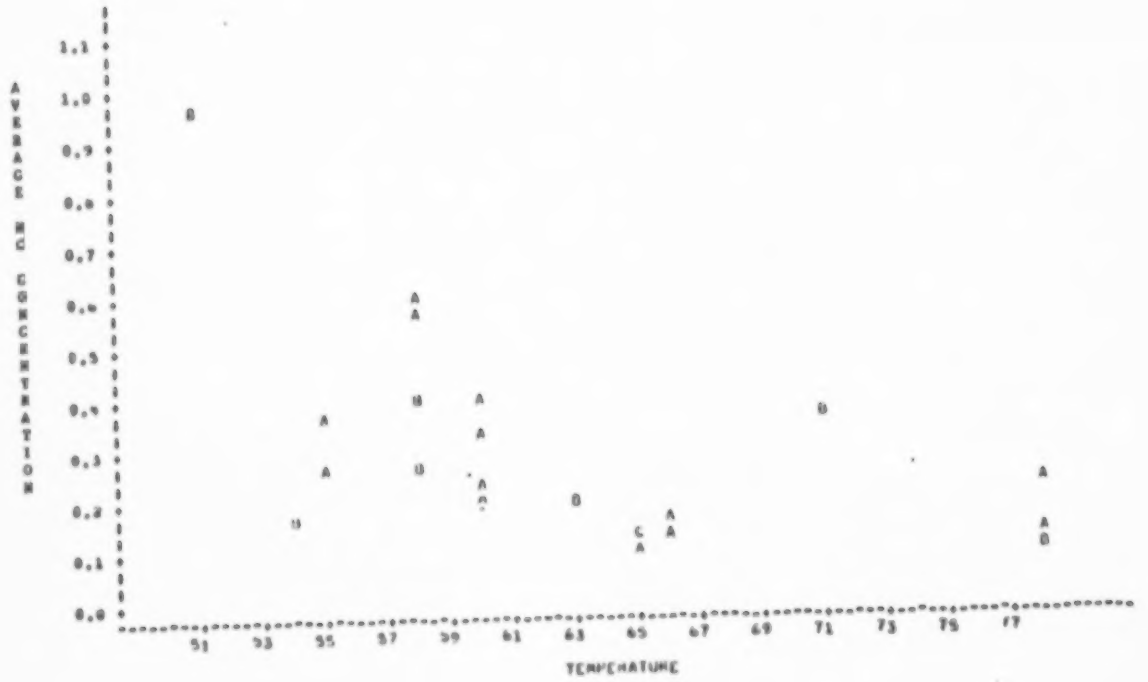


Figure A-5. NMHC Concentration Plotted as a Function of Temperature: Louisville Site
A = 1 Observation, B = 2 Observations, C = 3 Observations.

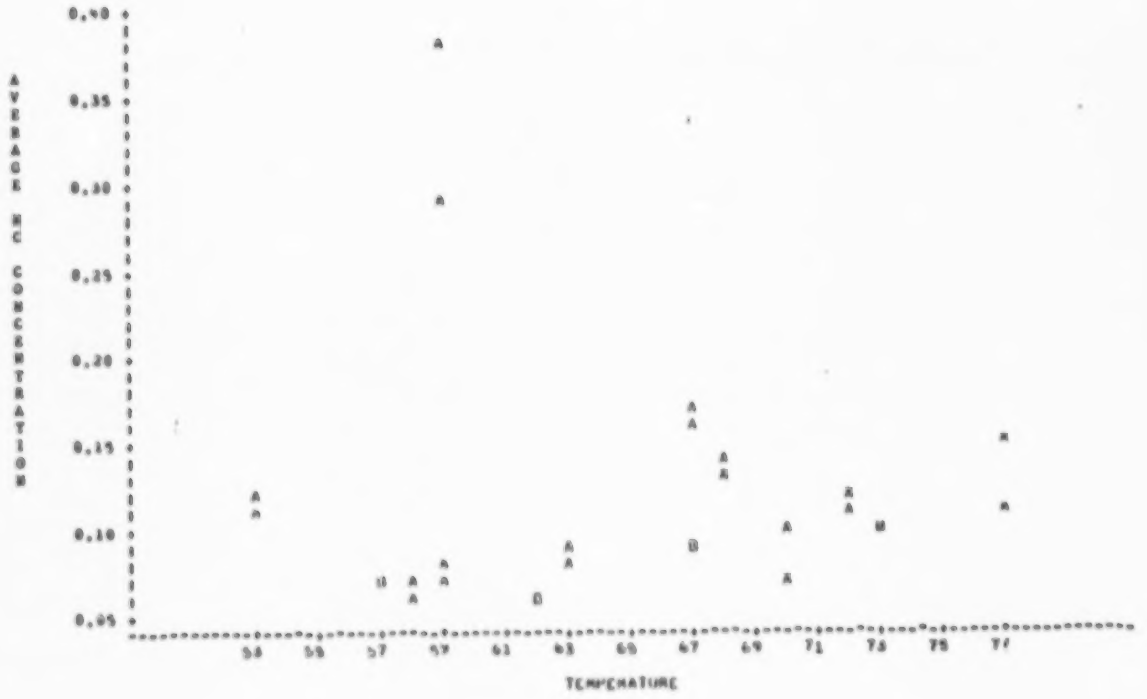


Figure A-6. NMHC Concentration Plotted as a Function of Temperature: Nashville Site
A = 1 Observation, B = 2 Observations, C = 3 Observations.

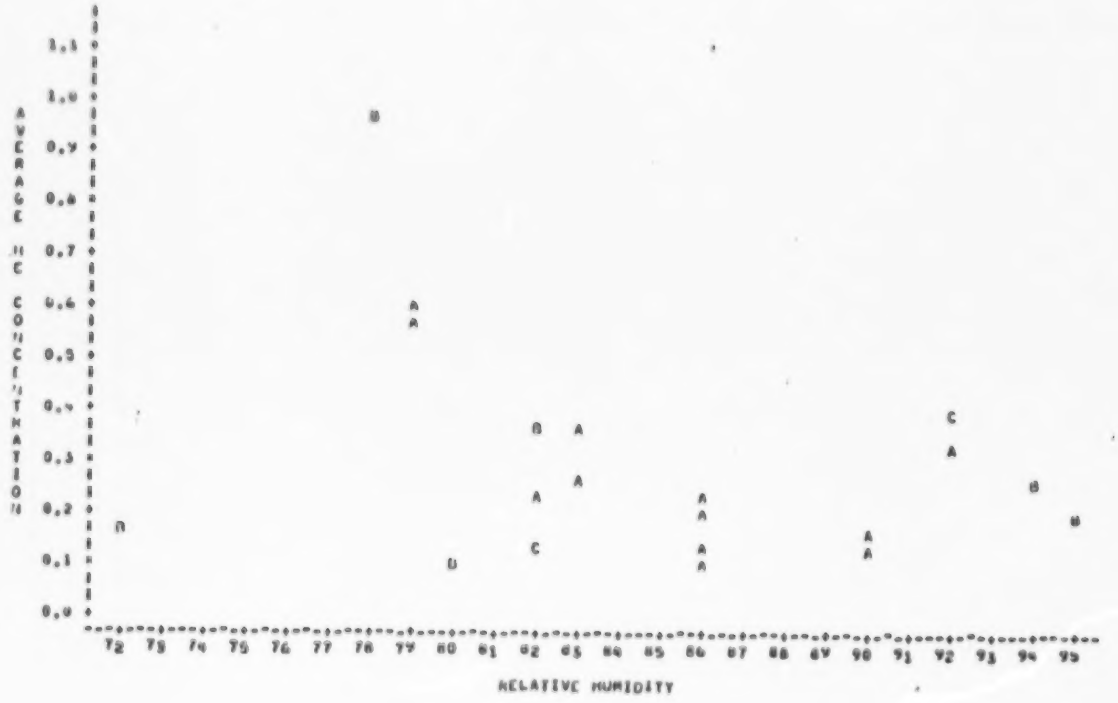


Figure A-7. NMHC Concentration Plotted as a Function of Humidity: Louisville Site
A = 1 Observation, B = 2 Observations, C = 3 Observations.

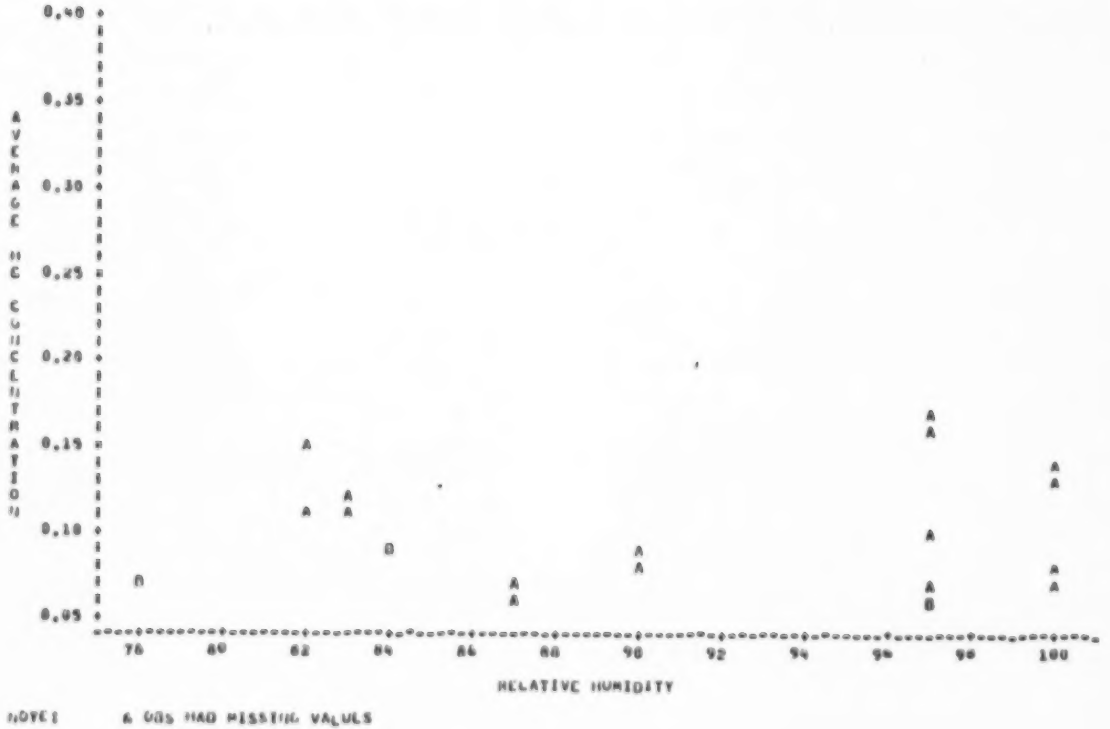


Figure A-8. NMHC Concentration Plotted as a Function of Humidity: Louisville Site
A = 1 Observation, B = 2 Observations, C = 3 Observations.

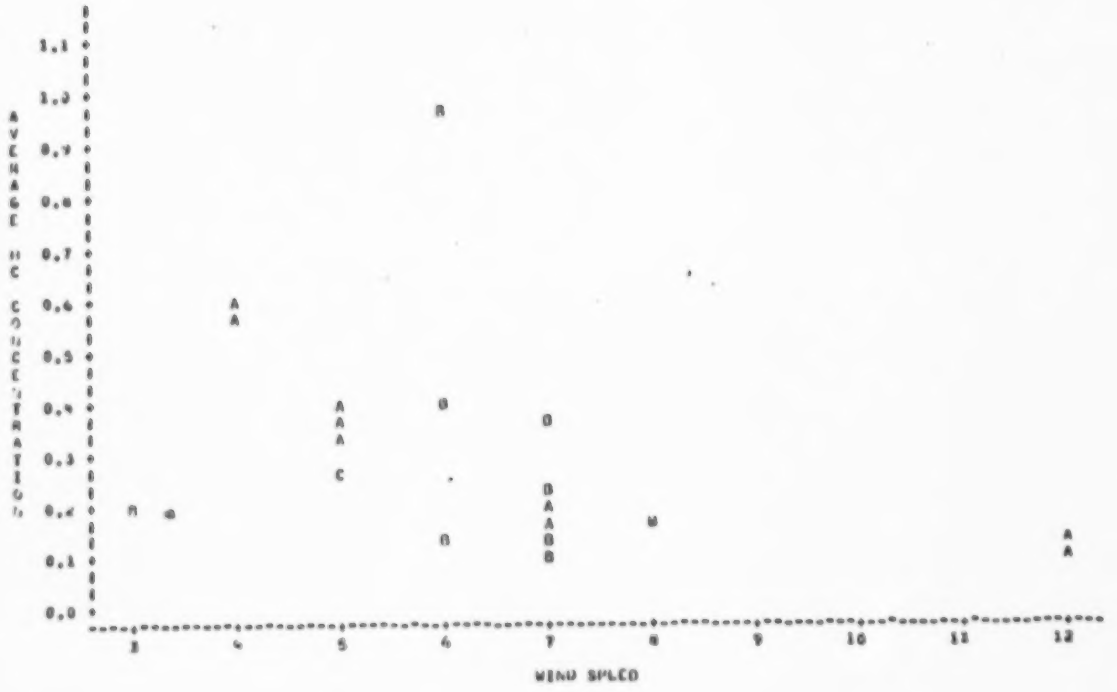


Figure A-9. NMHC Concentration Plotted as a Function of Wind Speed: Louisville Site
A = 1 Observation, B = 2 Observations, C = 3 Observations.

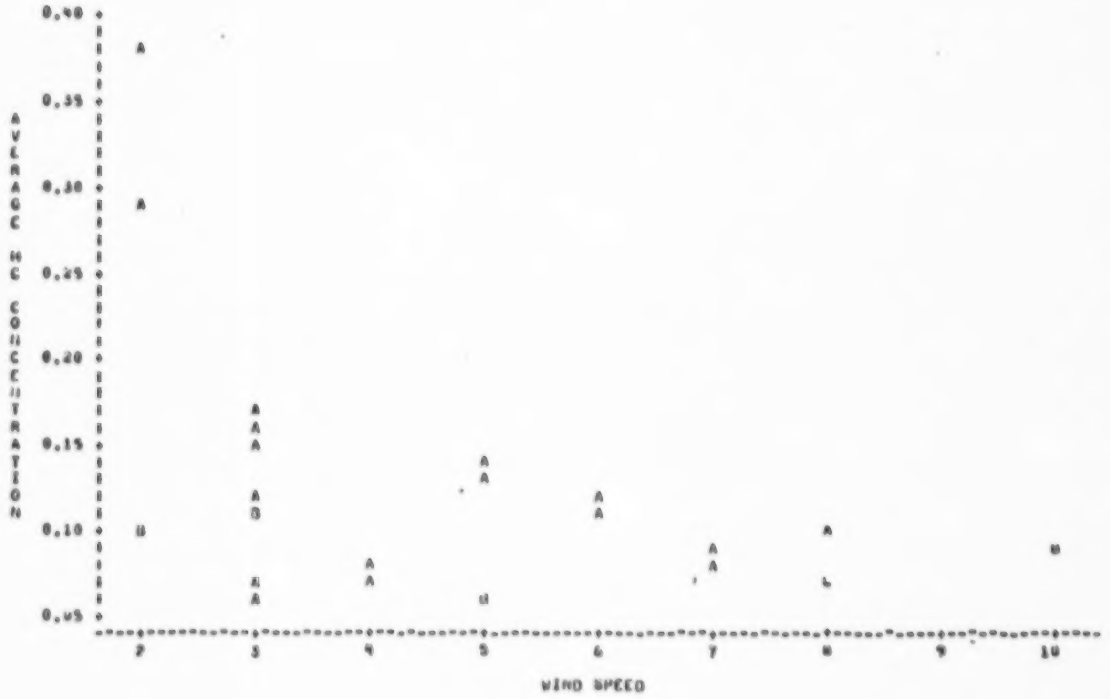


Figure A-10. NMHC Concentration Plotted as a Function of Wind Speed: Nashville Site
A = 1 Observation, B = 2 Observations, C = 3 Observations.

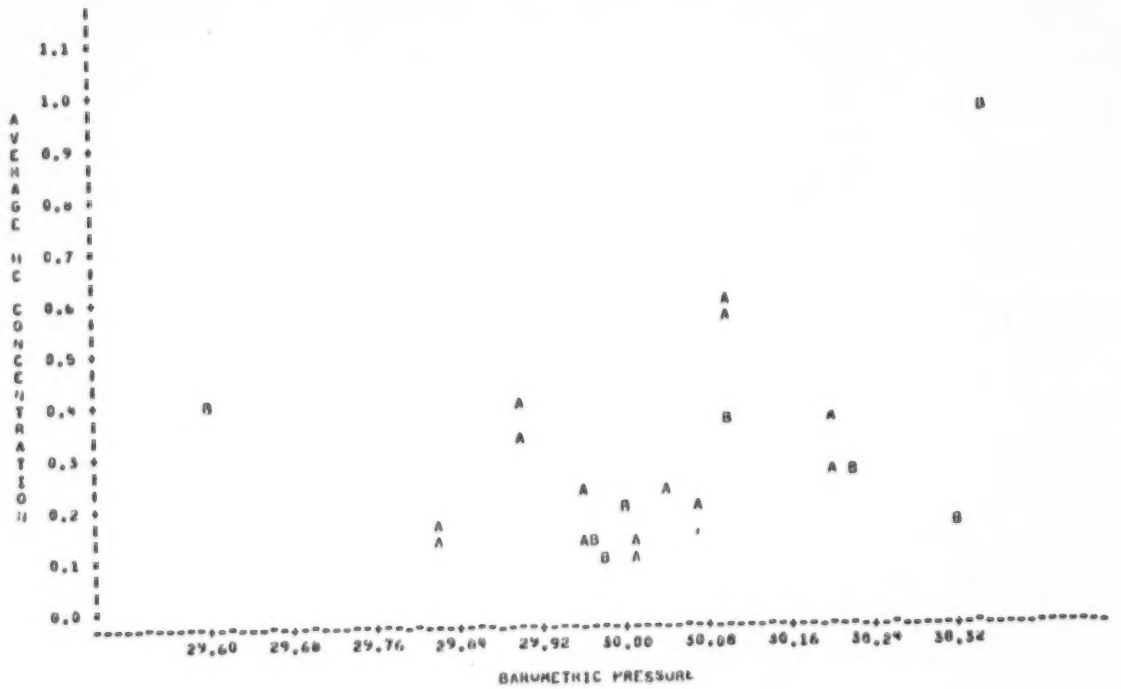


Figure A-11. NHMC Concentration Plotted as a Function of Barometric Pressure: Louisville Site. A = 1 Observation, B = 2 Observations.

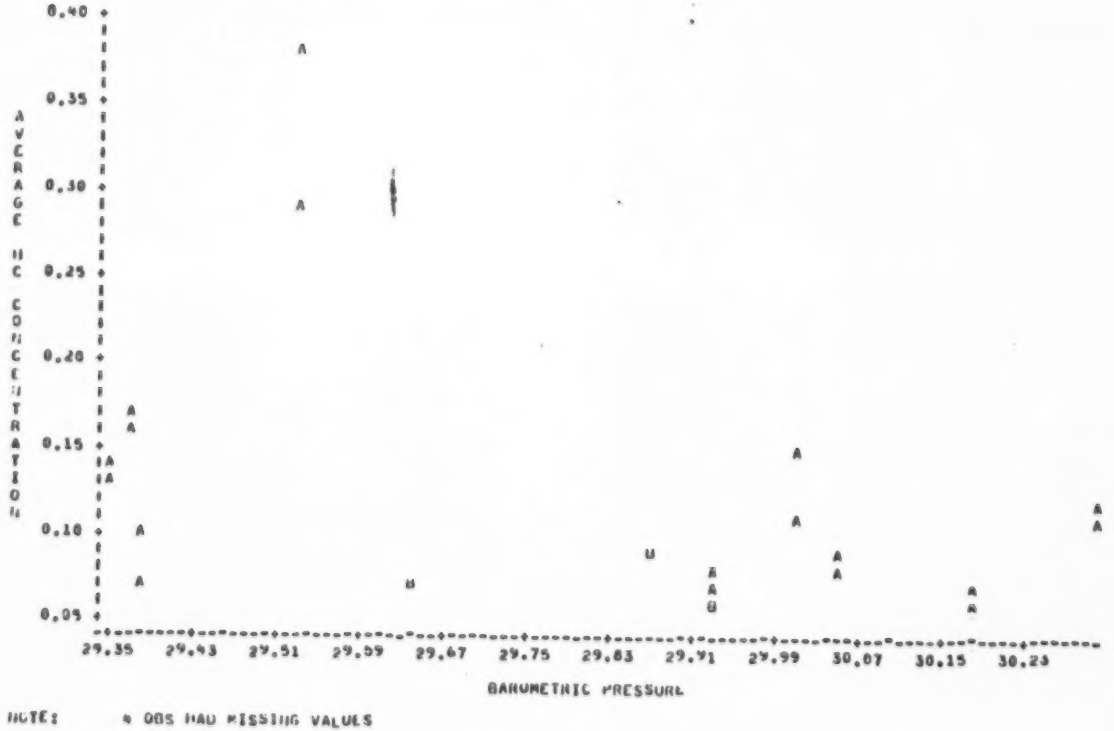


Figure A-12. NMHC Concentration Plotted as a Function of Barometric Pressure: Nashville Site. A = 1 Observation, B = 2 Observations.

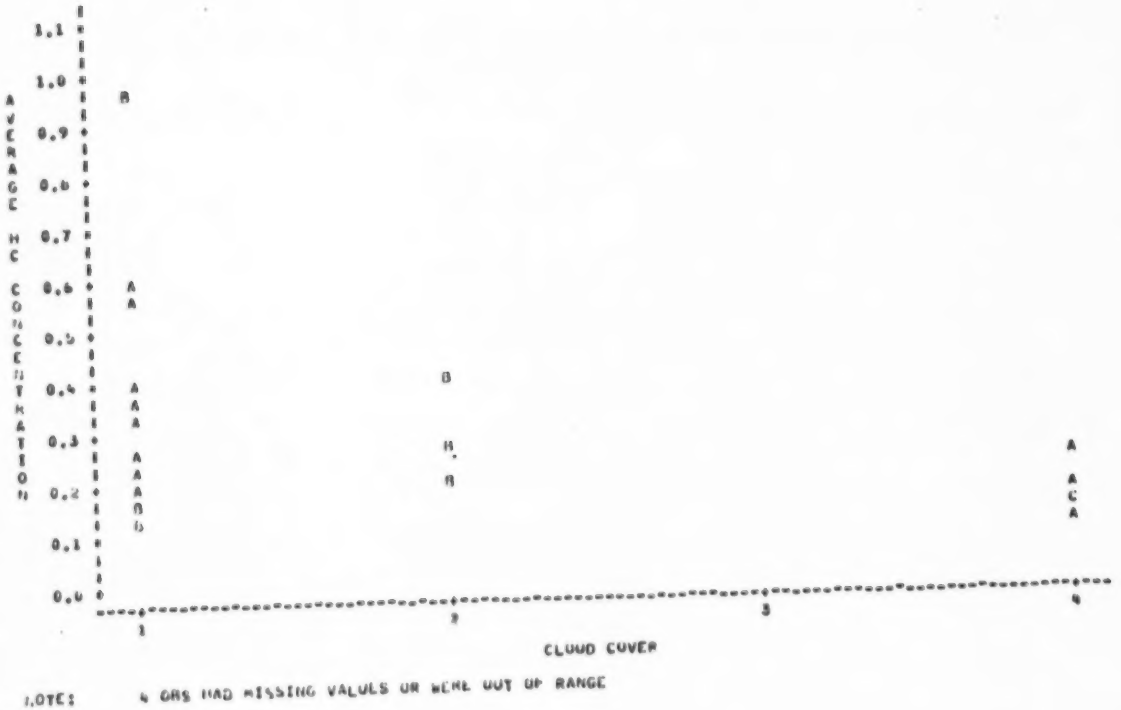


Figure A-13. NMHC Concentration Plotted as a Function of Precipitation: Louisville Site. 1 = Clear, 2 = Fog, 3 = Overcast, 4 = Rain. A = 1 Observation, B = 2 Observations, C = 3 Observations.

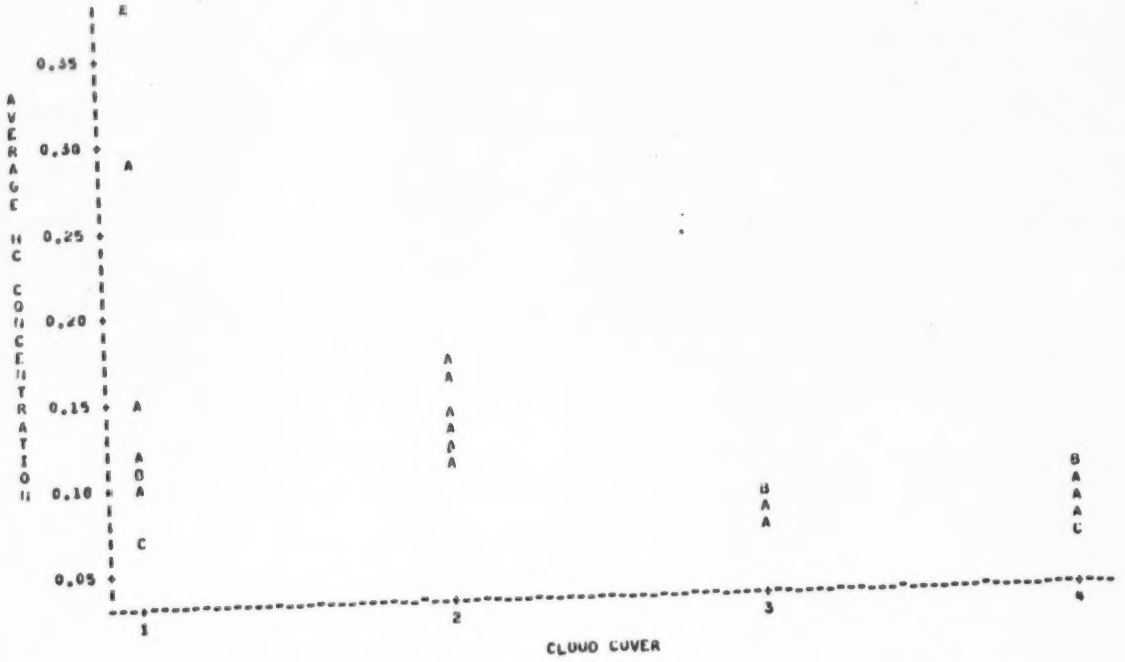


Figure A-14. NMHC Concentration Plotted as a Function of Precipitation: Nashville Site. 1 = Clear, 2 = Fog, 3 = Overcast, 4 = Rain; A = 1 Observation, B = 2 Observations, C = 3 Observations.

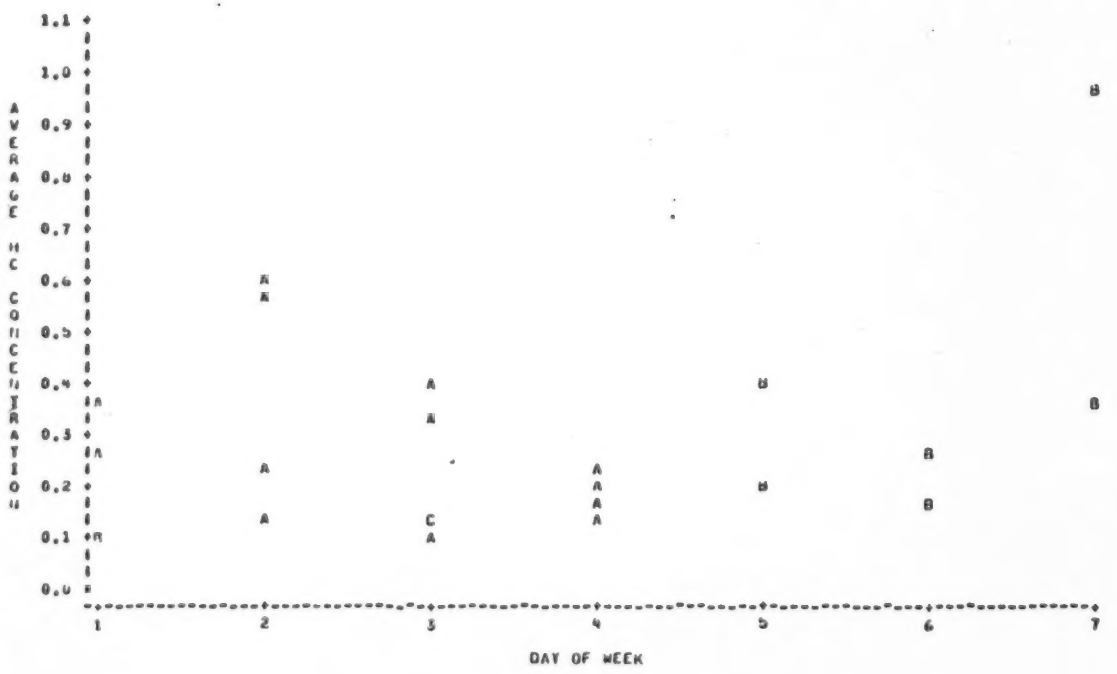


Figure A-15. NMHC Concentration Plotted as a Function of Day of Week: Louisville Site. 1 = Sunday, 2 = Monday, 3 = Tuesday, 4 = Wednesday, 5 = Thursday, 6 = Friday, 7 = Saturday; A = 1 Observation, B = 2 Observations, C = 3 Observations.

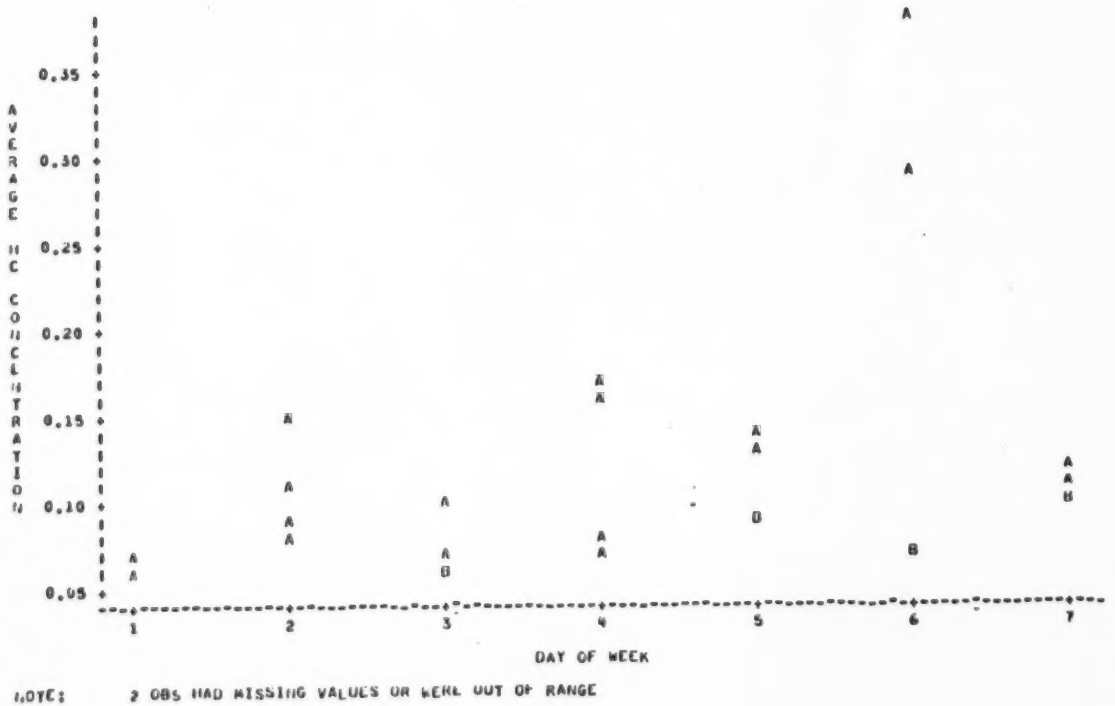


Figure A-16. NMHC Concentration Plotted as a Function of Day of Week: Nashville Site. 1 = Sunday, 2 = Monday, 3 = Tuesday, 4 = Wednesday, 5 = Thursday, 6 = Friday, 7 = Saturday; A = 1 Observation, B = 2 Observations, C = 3 Observations.

TABLE A-1. CORRELATION COEFFICIENTS[1] FOR RELATIONSHIPS BETWEEN NMHC CONCENTRATIONS AND WEATHER CONDITIONS

Correlation	Site	Relative Temperature	Humidity	Wind Speed	Pressure
Pearson	L	-0.5362	-0.1942	-0.3285	-0.3313
Probability	L	0.0023	0.3039	0.0764	0.0737
Spearman	L	-0.6113	-0.0076	-0.5405	0.3040
Probability	L	0.0003	0.09681	0.0021	0.1025
Pearson	N	-0.0199	0.1300	-0.4302	-0.3768
Probability	N	0.9199	0.5642	0.0223	0.0695
Spearman	N	0.3381	0.0688	-0.4661	-0.3563
Probability	N	0.0785	0.7611	0.0124	0.0874

[1]The Pearson correlation coefficient for random variable x and y is defined as:

$$\frac{\Sigma(x-\bar{x})\ (y-\bar{y})}{\left[\Sigma(x-\bar{x})^2\ \Sigma(y-\bar{y})\right]^{\frac{1}{2}}}$$

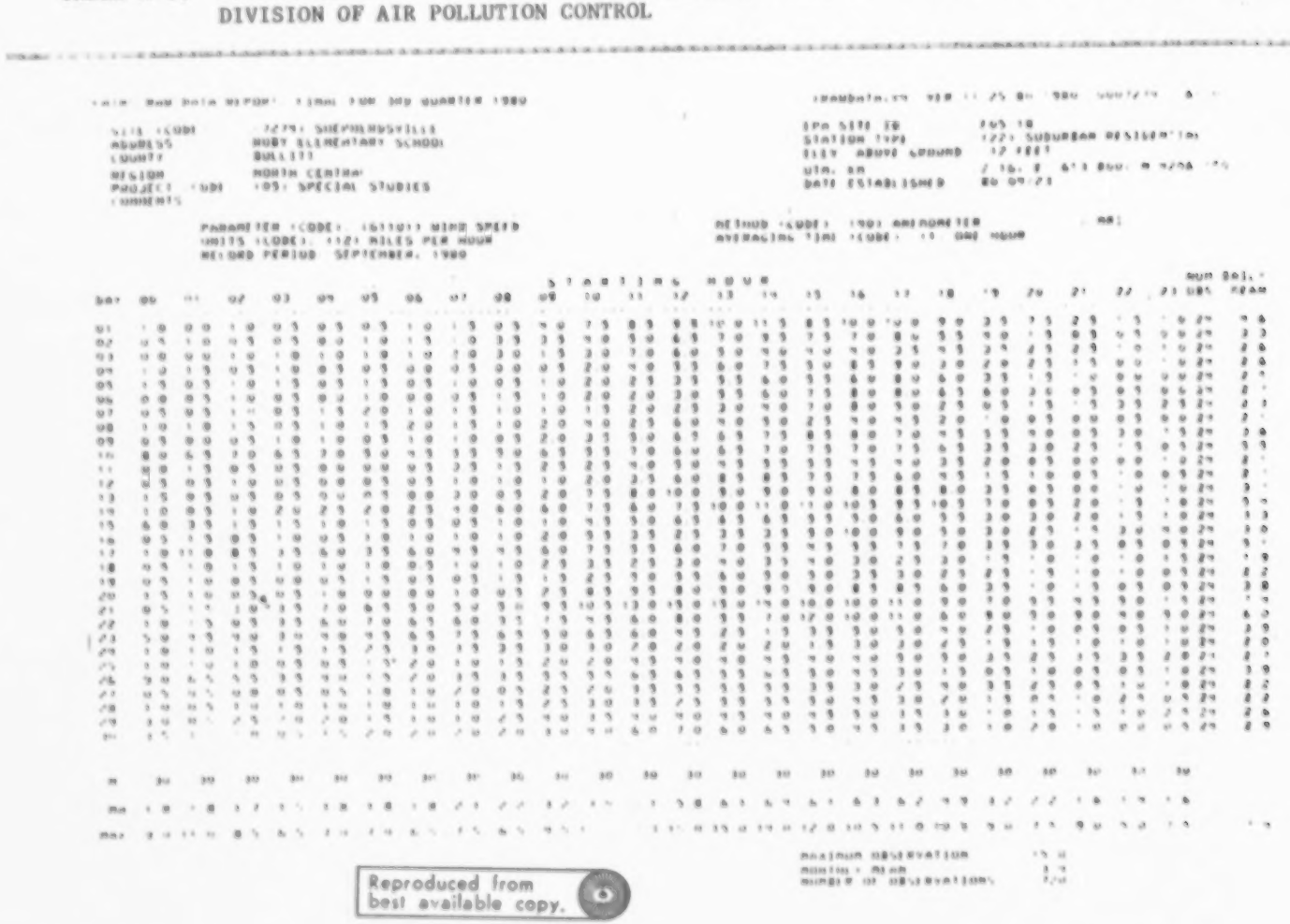
Where $\bar{x}$ and $\bar{y}$ are the sample means of x and y respectively. Its square is interpretable as the fraction of the variance of either of the variables which can be explained or predicted in terms of the other.

The probability associated with each correlation in Table A-1 is the probability that as large a correlation as the one observed or larger would have been observed if the two variables were actually unrelated. Thus, if the probability is small (say, less than 0.05), then one can be reasonably sure that the two variables are statistically related.

The Spearman correlation coefficient is the same as the Pearson coefficient except that the ranks of the variable, rather than the original data values, are used. The Spearman correlation is much less sensitive to extreme values than is the Pearson correlation. The fact that the Pearson and Spearman correlations are very similar suggests that there are no isolated extreme points which dominate the Pearson correlations.

TABLE A-2. WIND DIRECTION DATA COLLECTED AT THE SHEPARDSVILLE, KY SAMPLING SITE BY THE KENTUCKY DIVISION OF AIR POLLUTION CONTROL

TABLE A-3. WIND SPEED DATA COLLECTED AT THE SHEPARDSVILLE, KY SAMPLING SITE BY THE KENTUCKY DIVISION OF AIR POLLUTION CONTROL



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